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(71) Applicant *(for all designated States except US)*: CAMBRIDGE DISPLAY TECHNOLOGY LTD. [GB/GB]; 13 Station Road, Cambridge CB3 0DJ (GB).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: HOLMES, Andrew, Bruce [AU/GB]; 19 Newton Road, Cambridge CB2 2AL (GB). LI, Xiao-Chang [CN/GB]; 55 Silverwood Close, Cambridge CB1 3HA (GB). MORATTI, Stephen, Carl [NZ/GB]; 28 Owlstone Road, Cambridge CB3 9JH (GB). MURRAY, Kenneth, Andrew [GB/GB]; Flat 3, 16 Burlington Street, Bath BA1 2SB (GB). FRIEND, Richard, Henry [GB/GB]; 37 Barton Road, Cambridge CB3 9LG (GB).

(74) Agents: DANIELS, Jeffrey, Nicholas et al.; Page White & Farrer, 54 Doughty Street, London WC1N 2LS (GB).

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(57) Abstract

Optical devices fabricated from solvent processible polymers suffer from susceptibility to solvents and morphological changes. A semiconductive polymer capable of luminescence in an optical device is provided. The polymer comprises a luminescent film-forming solvent processible polymer which contains cross-linking so as to increase its molar mass and to resist solvent dissolution, the cross-linking being such that the polymer retains semiconductive and luminescent properties.

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POLYMERS FOR USE IN OPTICAL DEVICES

Field of the Invention

The invention relates to polymers for use in optical devices such as photoluminescent and electroluminescent devices.

Background to the Invention

Polymer LEDs were first described by Burroughes *et al* (PCT GB90/00584). Devices based on copolymers (Holmes *et al*, PCT GB91/01420; PCT GB91/01421) multilayers (PCT GB93/01573; PCT GB93/01574) and with high electron affinity polymers have also been reported (PCT GB94/01118).

Conjugated poly(3-alkylthienylene)s have been prepared, and reviewed by J. Roncali (*Chem Rev*, 1992, 92, 711) and applications in electroluminescent devices were reported by Y. Ohmori *et al*. (*Jpn. J. Appl. Phys. Part 2*, 1991, 20(11B),L1938-1940. Regioregular poly(3-alkylthienylene)s have been described by R.D. McCullough, R.D. Lowe, M. Jayaraman, and D.L. Anderson, (*J. Org. Chem.*, 1993, 58, 904). Solvent dependent chiroptical behaviour has been reported for regioregular poly(3-alkylthienylene)s M.M. Bouman, E.E. Havinga, R.A.J. Janssen and E.W. Meijer, *Mol. Cryst. Liq. Crist.*, 1994, 256, 439). Regiorandom hydroxy-functionalised polythiophene copolymers have been reported (C. Della Casa, E. Salatelli, F. Andreani and P. Costa Bizzarri, *Makromol. Chem. Makromol. Symp.*, 1992, 59, 233), and the potential for cross linking was noted (J. Lowe and S. Holdcroft, *Polym. Prepr.*, 1994, 35, 297-298).

More advanced polymeric LEDs can involve the use of both emissive and charge transport materials in order to improve the efficiency of the device [P.L. Burn, A.B. Holmes, A. Kraft, A.R. Brown, D.D.C. Bradley, R.H. Friend, *Mat. Res. Soc. Symp. Proc.*, 1992, **247**, 647; A.R. Brown, D.D.C. Bradley, J.H. Burroughes, R.H. Friend, N.C. Greenham, P.L. Burn, A.B. Holmes and A. Kraft, *Appl. Phys. Lett.*, 1992, 61, 2793; T. Nakano, S. Doi, T. Noguchi, T. Ohnishi Y. Iyechika, Sumitomo Chemical Company Limited, U.S.P. 5,317,169, May 31 1994].

Emissive polymers are the main active layer in polymer LEDs. Singlet excitons are formed under double charge injection which then decay radiatively to produce light emission. On the other hand, charge transport polymers have also been found to play an important role in enhancing the internal quantum efficiency of devices (photons emitted per electron injected), decreasing working voltages and in increasing the life-time of the devices. This was first shown by use of the known charge transporting molecule (PBD) [2-(4-biphenyl)-5-(4-*tert*-butyl-phenyl)-1,3,4-oxadiazole] as a blend in poly(methyl methacrylate) as mentioned above [Burn *et al.*; Nakano *et al.*]. Recently, high efficiency (4%) blue electroluminescence has been achieved by means of charge-transporting layers using polyvinylcarbazole (PVK) as a hole-transporting material and PBD blended with poly(methyl methacrylate) (PMMA) as an electron transporting material in the multi-layer device [ITO/PVK/PQ(polyquinoline)/PBD+PMMA/Ca] [I.D.Parker, Q.Pei, M.Marrocco, *Appl.Phys.Lett.*, 1994, 65(10), 1272]. The role of the charge transport layer in LEDs include: (i) assisting effective carrier injection from the electrode to the emitting layer (ii) confining the carriers within the emitting layer and thus increasing the probability of recombination processes through radiative decay, leading to light emission (iii) preventing the quenching of excitons at the boundary between an emitting material and the electrode.

Most common conjugated polymers are more easily p-doped and thus exhibit hole-transport properties. On the other hand, electron transport and electron injection in polymer LEDs have proved to be more difficult and are thus required in order to improve device efficiency and performance.

An aromatic oxadiazole compound such as PBD is well known to be a useful electron transport material [K.Naito, *Jpn. Kokai Tokkyo Koho* , JP 05,202,011,1993 ; S.Lunak, M.Nepras, A.Kurfurst and J.Kuthan, *Chem.Phys.*, 1993, 170, 67]. Multi-layered LED devices with improved efficiency have been reported using evaporated PBD or a spin-coated PBD/PMMA blend as an electron transport layer.

In each case, however, problems that will lead to device breakdown (such as the aggregation and re-crystallisation of PBD) may be expected to occur under the influence of an electrical field or temperature increase when the device is working [C.Adachi, *et al*, *Jpn. J. Appl. Phys.*, 1988, **27**, L269; C. Adachi, S. Tokito, T. Tsutsui, S. Saito, *Jpn. J. Appl. Phys*. 1988, **27**, L713; Y. Hamada, C. Adachi, T. Tsutsui, S. Saito, *Jpn. J. Appl. Phys*. 1992, **31**, 1812; K. Naito, A. Miura, *J.Phys.Chem.*, 1993, **97**, 6240].

Conjugated polymers that contain aromatic and/or heteroaromatic rings have enjoyed considerable interest because of their potential electrical conductivity after being doped and electroluminescent properties. However, there is a severe processibility problem for conjugated polymers as they are usually insoluble or infusible because of the rigidity of the main polymer chain and strong intermolecular forcesbetween polymer chains. One way to improve the processibility of these polymers is to prepare a soluble precursor which can then be converted into a rigid conjugated polymer, as can be done with poly(*p*-phenylenevinylene) (PPV) **(A)** [A green yellow emitter, prepared by the sulfonium precursor route: P.L. Burn, D.D.C. Bradley, R.H. Friend, D.A. Halliday, A.B. Holmes, R.W. Jackson and A. Kraft, *J. Chem. Soc., Perkin Trans.*, 1992, **1**, 3225]. Another way is to generate a fully conjugated material while increasing solubility by attaching bulky and flexible alkyl or alkoxy groups onto the main chain thereby weakening the intermolecular forces (as shown in the case of alkyl- or alkoxy-substituted PPV in **(B)** and **(C)**). A third way is to attach or insert a photoluminescent chromophore to a flexible polymer chain since the flexible chain segments will enhance the solubility in conventional organic solvents. This has been shown in the case of a block copolymer consisting of π-conjugated active blocks sandwiched between non-active flexible blocks [R.Gill, G.Hadziioannou, J.Herrema, G.Malliaris, R.Wieringa, J.Wildeman, WPI Acc..No.94-234969; Z. Yang, I. Sokolik, F.E. Karasz, *Macromolecules*, 1993, **26(5)**, 1188; Sumitomo Chem.Co.Ltd., JP

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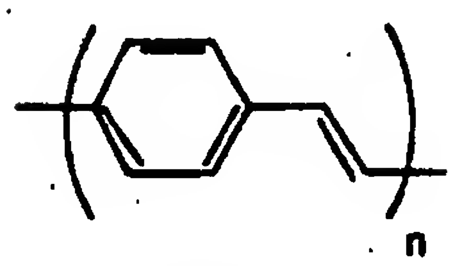
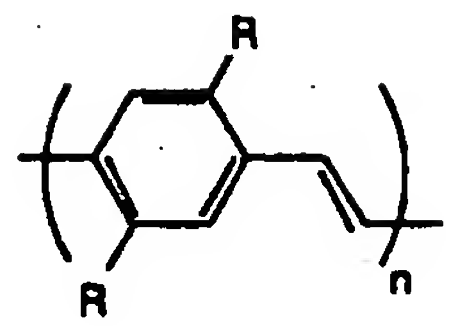


PPV

A



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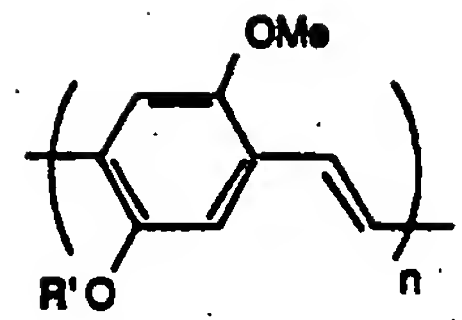


R' = 2-ethyl hexyl

C

In order to improve the performance of polymer LEDs, the luminescent polymer needs to be used in association with a charge transport polymer. Conventionally, charge transport materials may be used as single layers between the emitting layer and the electrodes. Alternatively, blends may be used.

Thus, prior art polymers used in optical devices suffer from susceptibility to solvents and morphological changes owing to low glass transition temperatures. Moreover, when molecular electron transport materials are used in such optical devices, problems involving the aggregation and recrystallisation of the material may lead to device breakdown.

Summary of the Invention

In one aspect, the present invention provides a semiconductive polymer capable of luminescence in an optical device, such as a photoluminescent or electroluminescent device. The polymer comprises a luminescent film-forming solvent processible polymer which contains cross-linking so as to increase its molar mass and to resist solvent dissolution, the cross-linking being such that the polymer retains semiconductive and luminescent properties.

By increasing the molar mass of the polymer the deleterious effects of susceptibility to solvents and morphological change owing to low glass transition temperatures are avoided. Surprisingly, the cross-linked polymers retain their semiconductive and luminescence properties. Luminescent and

electroactive polymer thin films such as those used in optical devices may therefore be stabilised. Because the thin films resist dissolution in common solvents this enables deposition of further layers of, for example, electroactive polymer films by solvent coating techniques thereby facilitating device manufacture. The cross-linked semiconductive polymers retain all their desirable luminescence properties and have the advantage of exhibiting enhanced morphological stability under device operation.

The cross-linking may be formed in the semiconductive polymer by thermal cross-linking, chemical cross-linking or photochemical cross-linking. Cross-linking methodology for polymers is well-known. For example, the cross-linking of polymers for photoresists by thermal, chemical and photochemical methods has been reviewed; (S. Paul, *Cross Linking Chemistry of Surface Coatings*, in *Comprehensive Polymer Science*, G. Allen (Ed.), Pergamon, Oxford, 1989, Vol. 6, Ch.6, pp. 149-192; S.R. Turner and R.C. Daly, *Photochemical and Radiation-sensitive Resists*, in *Comprehensive Polymer Science*, G. Allen (Ed.), Pergamon, Oxford, 1989, Vol. 6, Ch.7, pp. 193-225; S.P. Pappas, *Photocrosslinking* in *Comprehensive Polymer Science*, G. Allen (Ed.), Pergamon, Oxford, 1989, Vol. 6, Ch.5, pp. 135-148). In addition, an example of cross linking of polymers through ring opening metathesis polymerization of cyclooctene-5-methacrylate was reported by B.R. Maughon and R H Grubbs, (*Polym. Prepr.*, 1995, 36, 471-472).

A particularly useful example of thermal cross-linking involves the use of azide groups usually attached to the polymer main chain by a spacer group. At a temperature typically in the range of 80°C to 250°C the aliphatic azide will either form a pyrazoline adduct with a double bond or decompose to form a highly reactive nitrene which can then form cross-links with other polymers. An aryl azide will behave similarly in the range 20°C to 250°C. The spacer is advantageously non-rigid. Preferably the spacer comprises $-(CH_2)_n-$ or $-(CH_2)_n-Ar-$ in which

n is an integer preferably in the range 2 to 20 and Ar is an aryl group, preferably a phenylene group. A good example of such a spacer is a $-(CH_2)_{11}-$ group.

Chemical cross-linking may be effected using diisocyanates or activated dicarboxylic acid derivatives to react with terminal functional groups (e.g. -OH) on the soluble polymer. In this way urethane or ester linkages can be created. Alternatively, a low molecular weight bifunctional or polyfunctional compound (e.g. an epoxy resin) can be blended with the solvent processible polymer for the purpose of reacting chemically with existing functional groups (e.g. amino etc) in the polymer main chain or on the side chains of the polymer. Suitable cross-linking agents include formaldehyde or other aldehydes, bis or polyfunctional azides such as 1,6-bisazidohexane, and polyisocyanates.

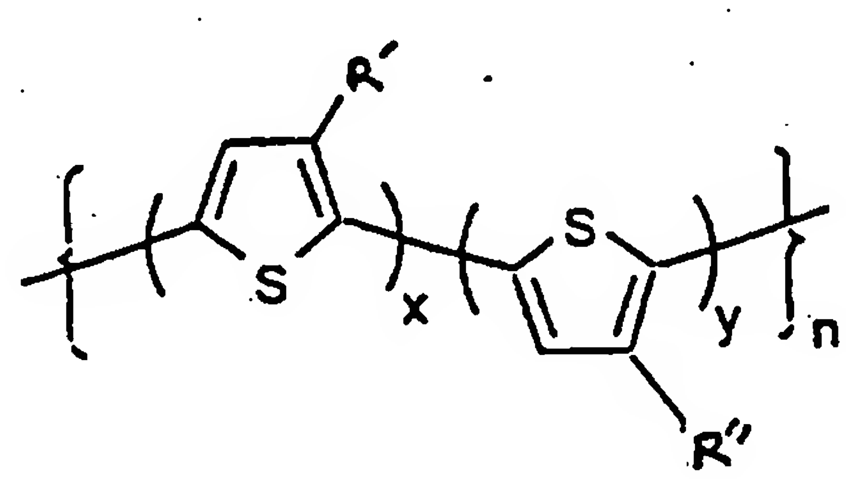
Photochemical cross-linking may be effected by any side chain substituent capable of becoming activated upon irradiation with light of appropriate energy, usually UV light. For example, cinnamate esters will undergo [2+2]-cycloaddition under appropriate conditions, typically irradiation of the polymer film at ambient temperature with a medium pressure Hg lamp. Also, photolysis of alkyl or aryl azides over a wide temperature range, preferably -50°C to +50°C, can generate reactive nitrene intermediates which can cross-link the polymer.

The luminescent film-forming polymer and the cross-linked form thereof according to the present invention may be luminescent either by virtue of a luminescent main chain or a luminescent side chain. The polymer may comprise any such film-forming polymer, including copolymers and oligomers. The luminescent main chain polymers have been described in PCT GB 90/00584 and PCT GB91/01420, for example. Such polymers include poly(arylene vinylene) derivatives. Particularly useful poly(arylenevinylene) polymers in the present invention include polymers of general formula B and which carry cross-linkable functionality as an attachment. Electroluminescent polyarylenes are also

particularly useful in the present invention, including polyheteoarylenes, especially the polythiophenes. Polythiophene copolymers are known to be capable of luminescence and substituted poly(3-alkyl thienylenes) are preferred.

Statistical copolymers of substituted poly(3-alkylthienylene)s containing regioregular head to tail linkages can be made according to K.A. Murray, S.C. Moratti, D.R. Baigent, N.C. Greenham, K. Pichler, A.B. Holmes and R.H. Friend, in *Synth. Met.*, 1995, 69, 395-396 and then cross-linked. The side chain alkyl substituents or a fraction thereof carry functionality which can be employed in chemical, photochemical or thermal cross-linking processes.

Further examples of polymers having a luminescent main chain are those which have the electroluminescent segments in scheme 2 below forming part of the polymer main chain. In a preferred embodiment of the invention, the polythiophene copolymer is of the general formula



in which R′ is a solubilising group, R" is a spacer group cross-linking the main chain to another polymer, and x, y and n are each integers, wherein x:y is in the range 19:1 to 1:2 and n is in the range 3 to 100.

Preferably, R′ is $-C_6H_{13}$.

Where the polymer includes a luminescent side chain, this side chain may incorporate any luminophoric group such as a species containing at least 3 unsaturated units in conjugation. Preferably the luminescent side chain comprises a distyryl

benzene. Where the polymer includes a luminescent side chain, there is no need for the main chain of the polymer itself to be luminescent but the polymer should be transparent to the emitted light. Various polymers may therefore be used to form the main chain. Especially useful polymers include polystyrenes, polyacrylates, polysiloxanes, and polymethacrylates which are preferred. Polymethacrylates are discussed in further detail below.

In one embodiment of the invention, the polymer further comprises a charge transport segment which is present in the polymer main chain or covalently linked thereto in a charge transport side chain.

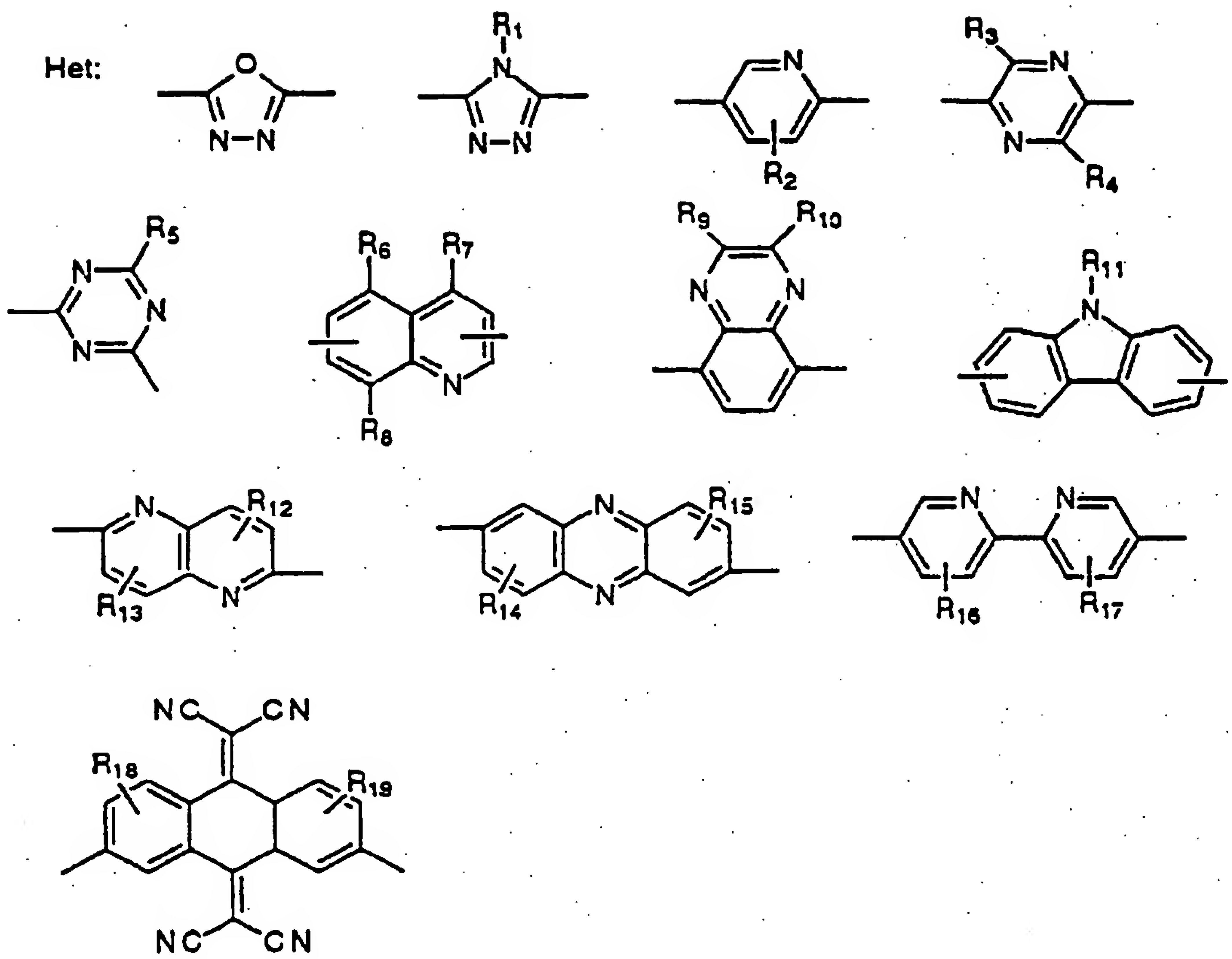
In a further aspect of the invention a polymer is provided which is capable of charge transport, preferably electron transport, in an optical device such as an electroluminescent device. The polymer comprises a film-forming polymer which is solvent processible or formed from a processible precursor polymer and which includes a charge transport segment in the polymer main chain or covalently linked thereto in a charge transport side chain.

The polymers may be used as both charge transporting and/or electroluminescent materials in polymer light emitting devices. The polymers may therefore include charge transport functional segments and electroluminescent functional segments either as a side chain group or in the main chain of the polymer. Precursor polymers leading, after a conversion step, to intractable final polymers may be used, as well as fully processible polymers. Each type of polymer can have specific advantages in processing multi-layered structures.

The charge transport segment may comprise the moiety Ar_1-Het-Ar_2 in which Ar_1 and Ar_2 are the same or different from one another and are aromatic units. Examples of these aromatic units are set out below in Scheme 1. Het is a heteroaromatic ring, the

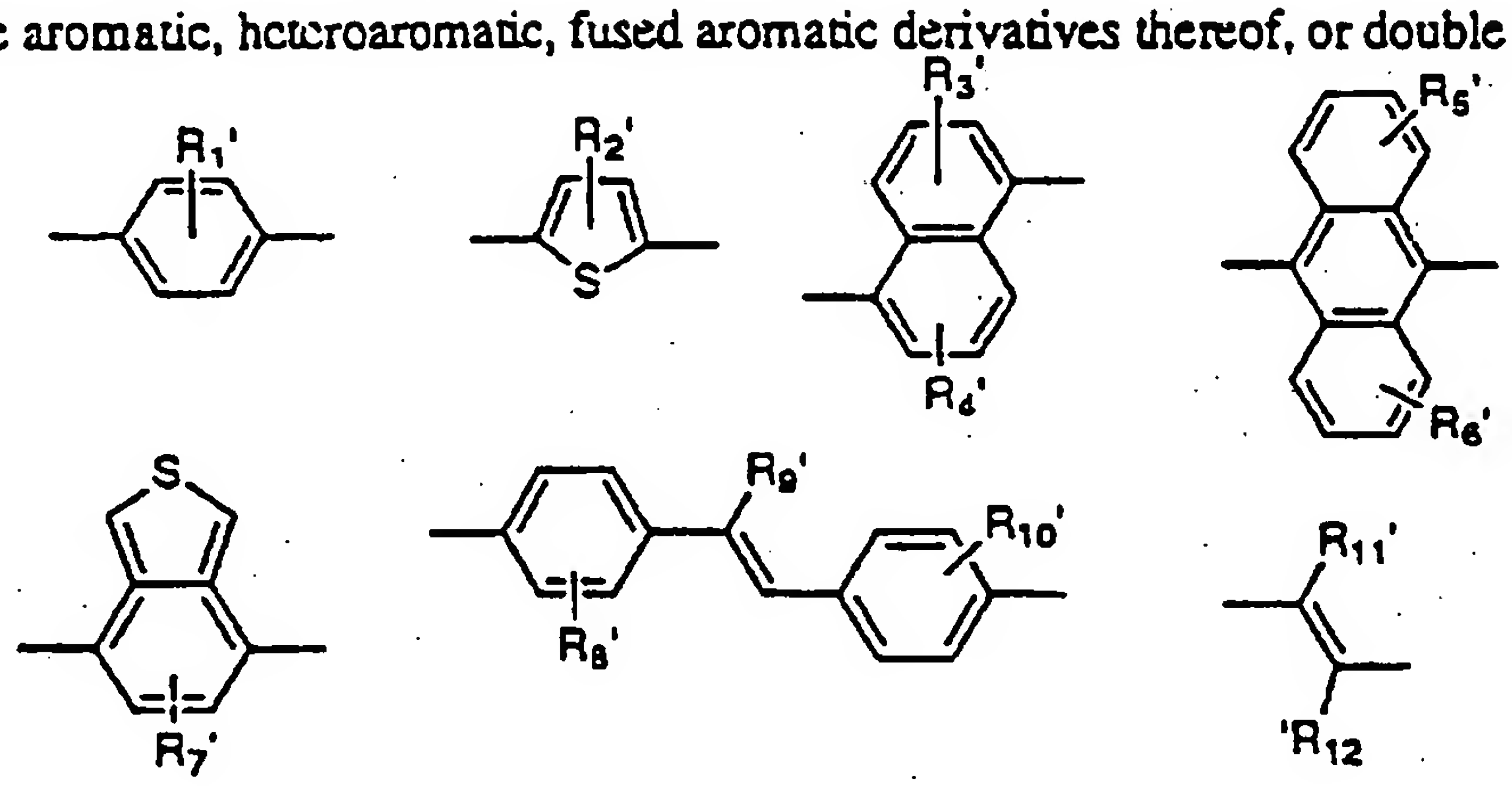
electronic structure of which favours charge transport. Examples include oxidiazole, thiadiazole, pyridine, pyrimidine and their benzo-fused analogues such as quinoline. Heteroaromatic rings which are electron deficient and therefore enhance charge injection and transport are generally useful.

Het:



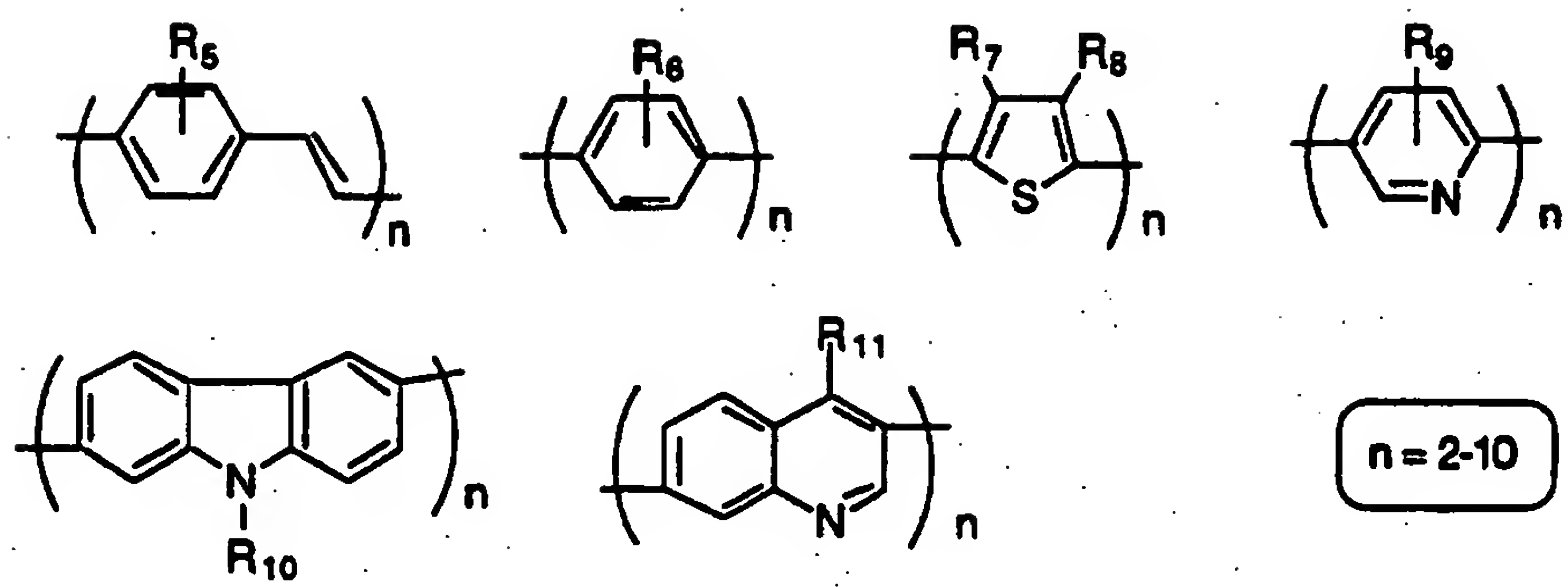
Ar_1, Ar_2 are aromatic, heteroaromatic, fused aromatic derivatives thereof, or double bonds:

Ar_1, Ar_2:



R_{1-19} and R_{1-12} are groups selected from the groups consisting of hydrogen and halogen atoms and cyano, alkyl and alkoxy side chains.

Scheme 1 Representative charge transport segments



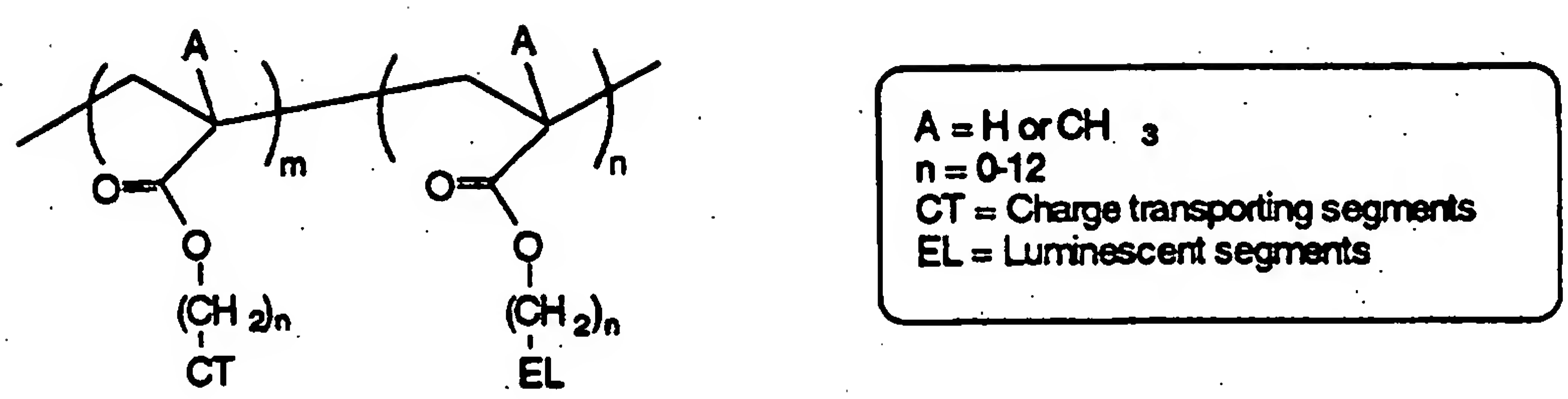
R_{5-11} = flexible alkyl or alkoxy solubilising and spacer groups

Scheme 2 Representative Electroluminescent Segments

The electroluminescent segments may comprise conjugated photoluminescent chromophore segments as illustrated in Scheme 2.

The side chain (co)polymer consists of any backbone polymer containing side chain modifications with luminescent and/or electron transporting segments. A typical example is a poly(methacrylate) that contains charge transport segments and/or luminescent segments in the pendant side group as shown in Scheme 3.

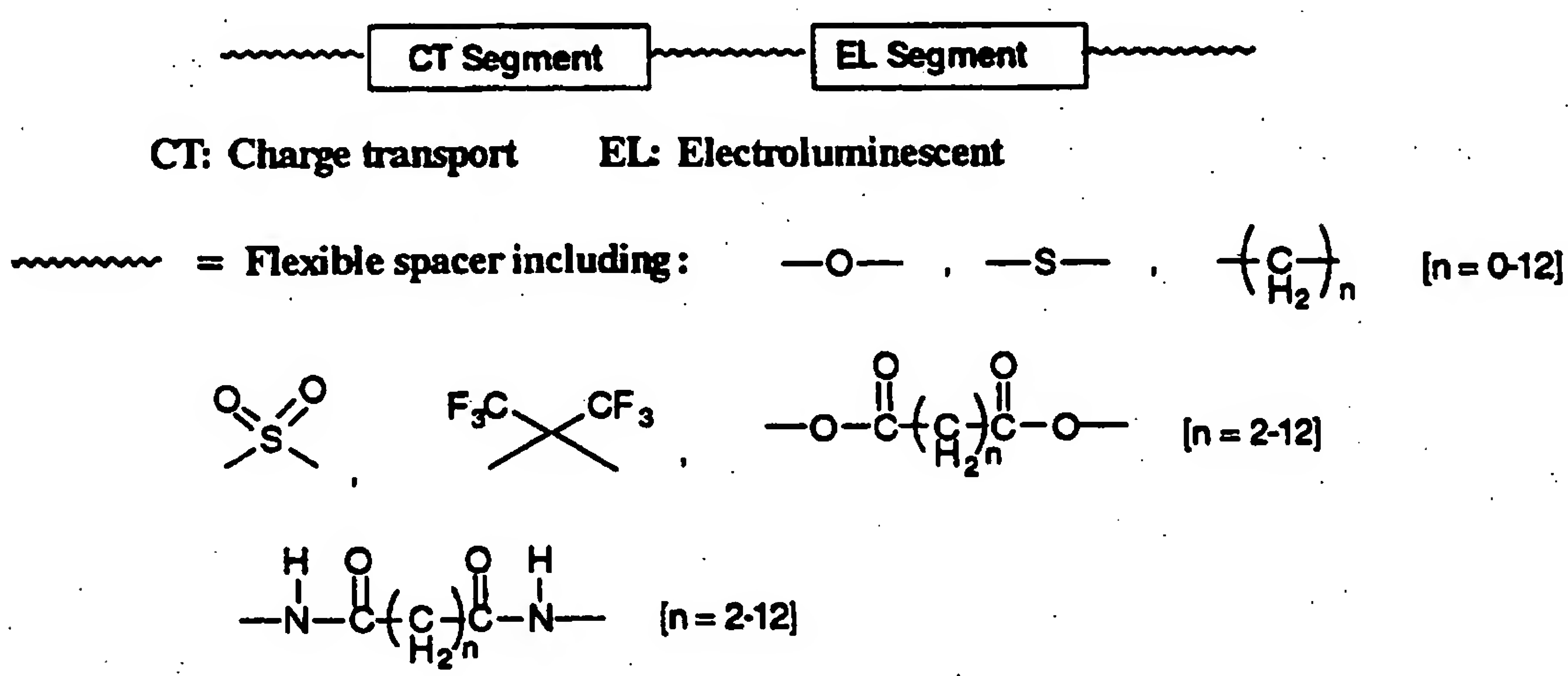
The side chain polymer may contain an optional third functional segment that will play a cross-linking role so as to improve the stability of the poly(methacrylate) i.e. by raising the glass transition temperature (T_g). The third segment may be a chemically cross-linkable group such as an epoxide, a thermally cross-linkable group such as an azide, or a photocross-linkable group such as a cinamate or a stilbene group.



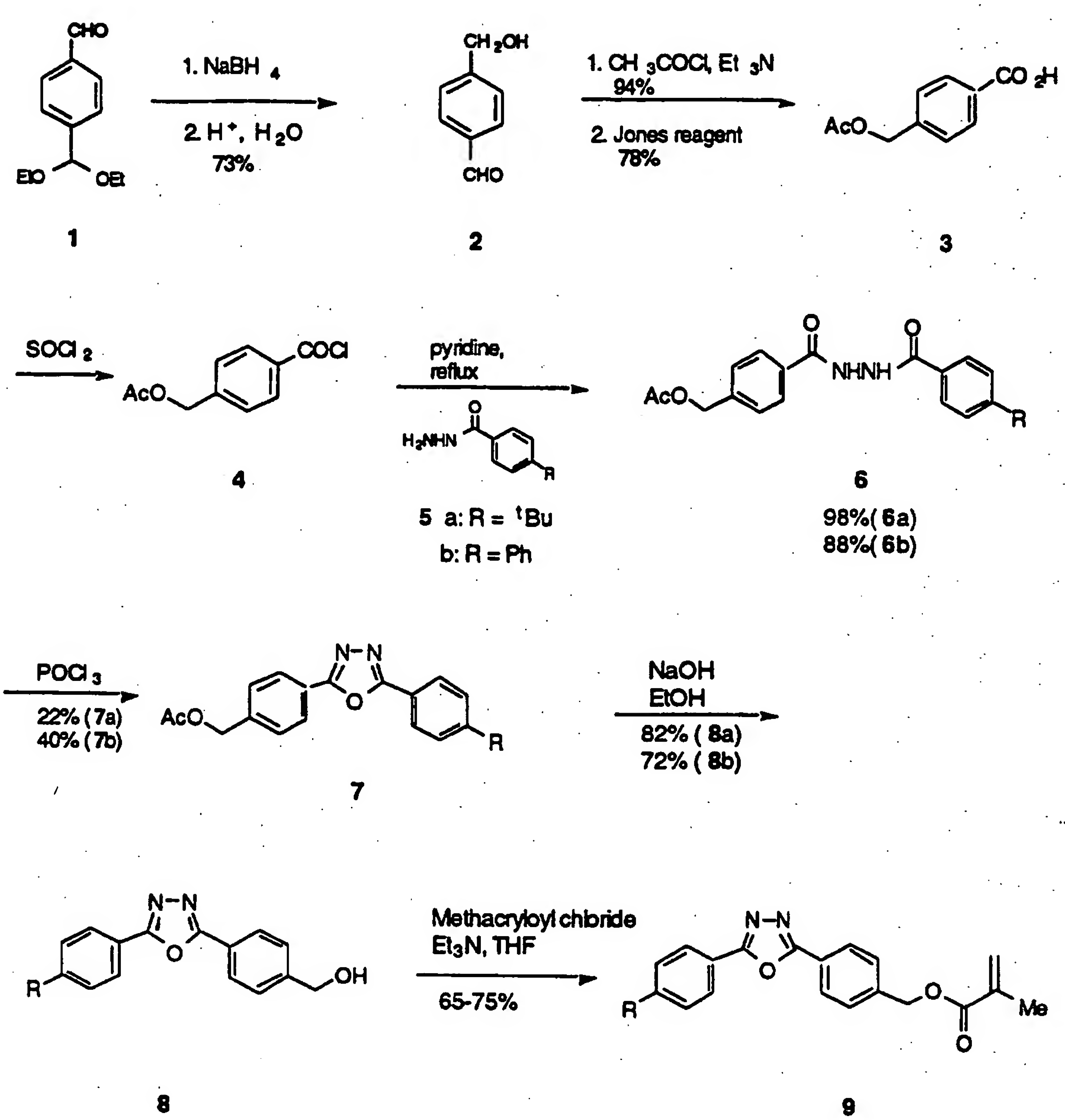
Scheme 3 Illustration of a side chain copolymer (using poly(methacrylate) as an example)

The main chain polymers and copolymers referred to herein are (co)polymers that contain transport segments and/or electroluminescent segments along the polymer or copolymer backbone with or without flexible spacers as illustrated by a representative example in Scheme 4.

The polymers described in the present invention are particularly suitable for use as electron transport layers in a multilayer LED device either as a blend with another electroluminescent polymer or as one of the components in a copolymer with another electroluminescent segment. This improves both the internal quantum efficiency and device performance.



Scheme 4 Representative Main Chain Polymer Structures

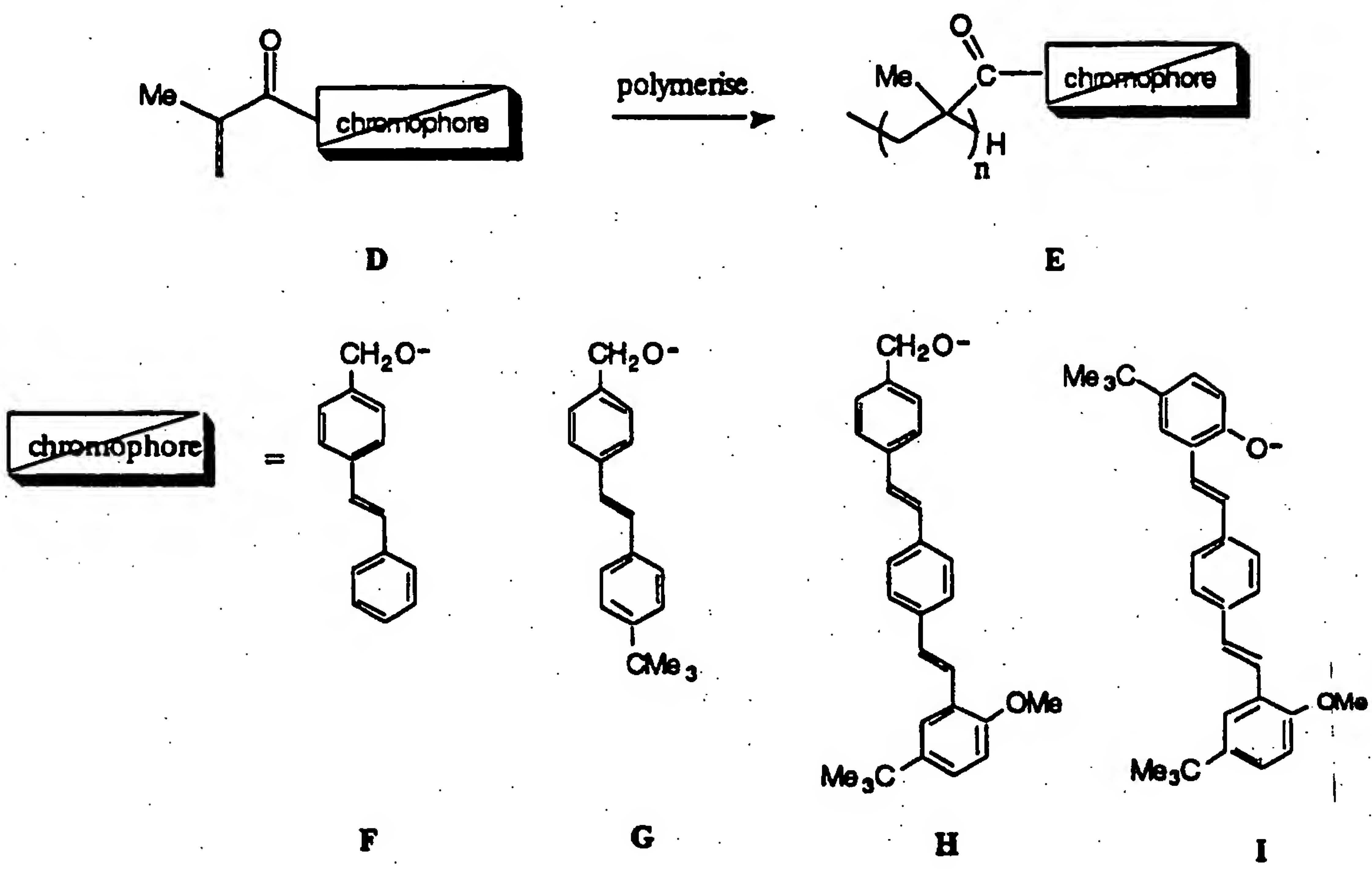


Scheme 5: Synthesis of oxadiazole monomers

PREPARATION AND APPLICATION OF SIDE CHAIN POLYMERS

Poly(methacrylates) have many advantages such as high transparency, high resistance to chemicals, and good mechanical strength. It is also relatively easy to synthesise high molecular weight polymers as well as multi-functional copolymers.

To illustrate this general concept, a range of aromatic oxadiazole bonded polymers [especially poly(methacrylates)] have been synthesised and investigated incorporating monomers as shown in Scheme 5. These (co)polymers can be used in association with emissive polymers in different ways (single layer, blended layer and copolymer layer) to give devices with improved performance.



Scheme 6 A Poly(methacrylate) Containing a Blue Light Emitting Side Chain

In a previous patent application (PCT/GB93/02856) a range of poly(methacrylate) derivatives containing chromophores D featuring blue emission were synthesised. The chromophoric groups F,G,H,I comprised two or three conjugated aryl rings (distyrylbenzene units) attached to the poly(methacrylate) chain via covalent linkages. This is a representative example of the numerous possibilities for blue side chain modified light emitting polymers. Crosslinking and copolymerisation with polymers carrying charge transporting segments make these

materials particularly attractive candidates for blue light emission.

The polymer capable of charge transport is generally used in an optical device as a functional polymer layer between an electroluminescent polymer layer and a charge injection electrode. This layer plays a role in enhancing charge and especially electronic injection from the metal electrode (usually a cathode) and charge transport. The polymer may balance the charge injection in a multi-layer polymer LED with improvement of device performance.

In a further aspect, the present invention provides use of a polymer as described above in an optical device, preferably an electroluminescent device. The present invention also provides an optical device which comprises a substrate and a polymer as defined above supported on the substrate. The optical device is preferably an electroluminescent device. Typically, the polymer is used in such devices as a thin film. In operation the cross-linked semiconductive polymers retain desirable luminescent properties and have the advantage of exhibiting enhanced morphological stability.

The present invention will now be described in further detail, by way of example only, with reference to the accompanying drawings in which:

FIGURE 1 shows a graph of internal quantum efficiency against current for the devices ITO/PPV/PMA-PPD/Ca and ITO/PPV/Ca;

FIGURE 2 shows a graph of current against field for the devices of Figure 1;

FIGURE 3 shows a graph of luminance L against voltage V for the device ITO/PPV/PMA-TPV+PMA-PPD/Ca;

FIGURE 4 shows a graph of efficiency against current for the

device of Figure 3;

FIGURE 5 shows a graph of luminance against wavelength lambda for the device ITO/PPV/PMA-TPV+PMA-PBD/Ca;

FIGURE 6 shows a graph of current against voltage for the device ITO/PPV/PMA-TPV-PBD/Al;

FIGURE 7 shows a graph of luminance against wavelength lambda for various LED devices ITO/PPV/Ca, ITO/PPV/Copolymer of 16 and 9b (1:1)/Al indicating cross-linking of the distyrlbenzene chromophore as a function of time;

FIGURE 8 shows a graph of efficiency against current for the device ITO/PPV/copolymer/Al of Figure 7;

FIGURE 9 shows a graph of luminance against wavelength lambda for the copolymer device of Figure 7;

FIGURE 10 illustrates representative polythiophenes for cross-linking;

FIGURE 11 shows cross-linking of a 9:1 copolymer 45b before and after heating;

FIGURE 12 shows a graph of a UV-VIS absorption spectrum of copolymer 49;

FIGURE 13 shows a photoluminescence spectrum of polymethacrylate 49 (p=0.5, q=0.3, r=0.2) with three functional groups;

FIGURE 14 shows a UV-VIS absorption spectrum of the 3-unit copolymer of Figure 13 upon exposure to UV light as a function of time;

FIGURE 15 shows an electroluminescent spectrum of a light emitting device using polymer 49 as an emissive layer

(ITO/polymer 49/Ca, with internal quantum efficiency of 0.1%);

FIGURE 16 shows graphs of current and luminance against voltage for a cross-linked polythiophene (45b, 9:1) device; and

FIGURE 17 shows an electroluminescent spectrum of a cross-linked thiophene device of Figure 16.

Example 1

The synthesis of methacrylate-PPD monomer (9a) - Scheme 5

Preparation of aldehyde (2): Sodium borohydride(4.9 g, 0.13 mol) pellets were added to a solution of terephthaldehyde mono-(diethyl acetal) (39.9g, 0.19 mol) in MeOH(150 ml) at 0 °C (using an ice bath). The reaction mixture was stirred for 1.5h at 0 °C. Water(100 ml) and HCl(10M, 200 ml) were added and the mixture stirred at room temperature for 1.5h. After removing MeOH under reduced presure, ethyl acetate(200 ml) was added. The organic layer was washed with sodium hydrogen carbonate solution and water. The clear organic layer was dried with anhydrous sodium sulfate. The crude product (20.35 g) was recrystallized from chloroform/hexane and was obtained as fine crystals(18.79 g, 73 %); m.p.43-45 °C.

Preparation of 4-(acetyloxy-methyl)benzoic acid (3): Triethylamine (15.4 ml, 110.4 mmol) was added to a solution of aldehyde (2) (12.57 g, 92.4 mmol) in THF (50 ml) and cooled to 0 °C. Acetyl chloride (7.91 g, 110.4 mmol) was then gradually added over 25 minutes, and the mixture was then left to stir for two hours at room temperature. After one hour, ethyl acetate (200 ml) was added and the solution washed with sodium carbonate (100 ml), HCl (17 %, 50 ml) and water (100 ml) respectively. The organic layer was then dried over sodium sulfate and the solvent removed under reduced pressure to give an oil which crystallised when cooled. Re-crystallisation in methanol-hexane gave light yellow crystals.

4-[acetyloxy-methyl]benzaldehyde: (15.39 g, 94 %). m.p. 33-35 °C; R_f 0.62 (ether). ν_{max} (KBr)/cm^{-1}: 1735 s (O-C=O), 1686 s (H-C=O), 1608 m (phenyl absorption), 1384, 1369, 1253, 1212, and 811; λ_H(250 MHz, $CDCl_3$) 2.10 (3 H, s, CH_3), 5.14 (2 H, s, CH_2O-), 7.41 (2 H, d, *J* 8.1, Ar-H), 7.89 (2 H, d, *J* 8.1, Ar-H) and 9.98 (1 H, s, CHO). δ_C (63.5 MHz; $CDCl_3$) 20.8 (CH3), 65.4 (CH_2), 128.2, 129.9, 142.7, 141.8 (phenyl carbons), 170.6 (O-C=O) and 191.8 (H-C=O).

4-[acetyloxy-methyl]benzaldehyde (15.3 g, 86.5 mmol) in acetone (250 ml) was then reacted with Jones reagent (33.0 ml, a three-fold excess) while stirring (exothermal reaction). This was stirred for 2h before filtering out the green solid. The green solid was then dried under reduced presure and dissolved in ethyl acetate (400 ml) and washed with sodium carbonate solution and water until neutral. After removal of solvent, a crop of yellow crystals (13.3 g) was obtained which was then recrystallised in chloroform-hexane to give a white crystal (3) (12.62 g, 76%). m.p. 120-123 °C; R_f 0.29 (1:1 Hexane-ether v/v).

Preparation of 4-*tert*-butyl benzoic hydrazide (5a): Hydrazine hydrate (9.4 ml, 194 mmol) was added to methyl 4-*tert*-butyl benzoate (25.3 g, 29 mmol) in ethanol (25 ml) and then refluxed under nitrogen for 18h. The solvent was then removed under reduced pressure and the solid residue recrystallised from hot toluene-hexane (140 ml, 10:4 toluene-hexane v/v), to give colourless crystals of 4-*tert*-butyl benzoic hydrazide (19.25 g, 76%). m.p. 126-128 °C.

Preparation of 1-(p-*tert*-butyl benzoyl)-2-(4-acetyloxy-methyl-benzoyl)-hydrazine (6): Thionyl chloride (30 ml) was added to (3) (15.10g, 77.8 mmol) in a 250 ml three-neck RB flask and refluxed for 40 minutes at 70-80 °C. After removing the excess thinoyl chloride under vacuum, the brown oil (4) was then washed with chloroform (3X15 ml). The residue was then dissolved in dry pyridine (120 ml). Hydrazide (5a) (14.9g, 77.8 mmol) was at last added. The brown solution was stirred and refluxed for 3h before

pouring the mixture into ice water (700 ml) to precipitate the product which was then washed with water and dried at 80 °C *in vacuo* to give the product. The product can be further purified by recrystallisation in toluene to give white crystals. m.p.229-230 °C (with liquid crystal behaviour and easy decomposition in air); δ_H (250 MHz, $CDCl_3$) 1.32(9 H, s, ^tBu), 2.13(3 H, s, CH_3CO), 5.13(2 H, s, CH_2), 7.41(4 H, t) and 7.81(4 H, m, Ar-H), 9.59 and 9.72(2 H, d, -NHNH-); δ_C(63.5 MHz, $CDCl_3$) 20.9(CH_3), 31.1($C(CH_3)_3$), 65.4(CH_2), 125.7, 127.1, 127.6, 128.0, 128.3, 130.4, 131.1, 140.5(C), 156.1(C=O), 163.9 (C=O); ν_{max}($CHCl_3$)/cm^{-1}: 3233(N-H), 1736(O-CO), 1672(NH-CO), 1633, 1445, 1450(phenyl absorption); [Found: C, 68.66; H, 6.64; N, 7.65. $C_{21}H_{24}N_2O_4$ requires C, 68.48; H, 6.52; N, 7.61%].

Preparation of 2-(para-*tert*-butyl-phenyl)-5-(4-acetyloxy-methyl-phenyl)-1,3,4-oxadiazole (7a): $POCl_3$ (35 ml) was added to (6a)(3.31 g, 8.99 mmol) and refluxed for 18h under nitrogen. $POCl_3$ was distilled from the reaction mixture before pouring the residue into ice water. Extraction with ethyl acetate (2x200 ml) gave a yellow oil after removal of solvent. The crude product (TLC showed 3 spots) was purified by flash column chromatography using hexane-ether (10:1 to 3:7 v/v) yielding colourless crystals (7a) (1.02g, 22%). m.p. 93-95 ^{0}C; R_f 0.24 (1:1 hexane-ether v/v); δ_H (250 MHz, $CDCl_3$) 1.36 (9 H, s, ^tBu), 2.14 (3 H, s, CH_3CO), 5.18 (2 H, s, CH_2), 7.54 and 8.07 (4 H, m, Ar-H); σ_C (63.5 MHz, $CDCl_3$) 21.0 (CH_3CO), 31.1 ($C(CH_3)_3$), 35.1 ($C(CH_3)_3$), 66.5 (CH_2), 121.1 and 126.1, 126.8, 139.7(Ar-CH_2OAc), 123.9, 127.1, 128.6, 155.5(Ar-^tBu), 164.1(C) and 164.8 (C) and 170.7 (C=O); [found: C, 72.12; H, 6.29; N, 8.10. $C_{21}H_{22}O_3N$ requires C, 72.0; N, 8.0; H, 6.3%]; *m/z* (EI) 350 (80), 335 (100%), 161 (30) and 43 (30) [Found: (M^+) 350.1630. $C_{21}H_{22}$O3N requires M, 350.1630].

Preparation of 2-(para-*tert*-butyl-phenyl)-5-(4-hydroxyl-methyl-phenyl)-1,3,4-oxadiazole (8a): Oxadiazole (7a) (0.67g, 1.91 mmol) was added to a solution of sodium hydroxide (0.11 g, 2.75 mmol) in ethanol (30 ml), and the mixture stirred for 2h. The mixture was poured into aqueous sodium bicarbonate (5%, 100 ml) and a

white precipitate which formed, was collected by filtration. The crude product (0.9g) was recrystallised from $CHCl_3$-hexane yielding colourless crystals (8a) (0.53 g, 91%). m.p. 115-116 °C; R_f 0.08 (1:1 hexane-ether v/v). $\nu_{max}(CHCl_3)/cm^{-1}$: 3308(OH), 2967(CH), 1615, 1552, 1495(Ar), 965(oxadiazole); δ_H(250 MHz, $CDCl_3$) 1.36 (9 H, s, $(C(CH_3)_3)$, 2.22 (1 H, t, OH), 4.79 (2 H, d, CH_2O), 7.53 and 8.06 (8 H, m, 2xAr-H); d_C (63.5 MHz, $CDCl_3$) 21.0 (CH_3CO), 31.1 ($C(CH_3)_3$), 35.1 ($C(CH_3)_3$), 64.5 (CH_2OH), 121.0 and 123.1 (aryl carbons bonded to oxadiazole ring), 126.1, 126.8, 127.1, 127.3(Ar), 144.7.0 (Ar-CH_2OH), 155.4 (Ar-^tBu), 164.1 and 164.8 (C); [Found: C, 74.08; N, 9.03; H, 6.52; $C_{19}H_{20}O_2N_2$ requires C, 74.0; N, 9.1; H, 6.5 %]; *m/z* (EI) 308 (55), 293 (100%), 161 (25) 135 (25), 116 (25) and 77 (25) [Found: (M^+) 308.1525. $C_{19}H_{20}O_2N_2$ requires *M*, 308.1525].

Preparation of monomer (9a) Triethylamine (1.0 ml, 41.0 mmol) was added to a solution of oxadiazole (8a) (0.61 g, 19.8 mmol) in THF (20 ml) and stirred under N_2. Methacryloyl chloride (0.9 ml, 84 mmol) was added slowly by syringe. The solution was stirred for 2h at room temperature . Cloudiness was observed. Ether (100 ml) was added and the mixture was washed with water (100 ml), HCl (2M, 100 ml), and brine (100 ml). The combined aqueous washings were then extracted with more ether (100 ml). The combined ether layers were dried over anhydrous sodium sulfate and the solvent removed under reduced pressure to give an off-white solid. R_f=0.38 (1:1 hexane-ether v/v). After purification using flash column chromatography with ether-hexane(1:1 v/v), and drying, (8a) was obtained as colourless crystals (0.67 g , 91%). m.p. 106-109 °C; $\nu_{max}(CHCl_3)/cm^{-1}$: 2966(C-H), 1720 s (C=O), 1615, 1494(Ar), 965 (oxadiazole); δ_H (250 MHz, $CDCl_3$) 1.36 (9 H, s, ^tBu), 1.99 (3 H, t, *J* 1.313, CH_3), 5.27 (2 H, s, CH_2), 5.63, 6.20(2 H, 2, CH=CH), 7.55 and 8.10 (8 H, m, 2 x Ar-H); XXXδ_C (100 MHz, $CDCl_3$) 18.3 (CH_3), 31.1 ($C(CH_3)_3$), 35.1 (CMe_3), 65.7 (CH_2-O), 121.0 and 123.8 (Ar), 126.1, 126.2, 126.8, 127.1, 128.4, 139.8 and 155.5 (Ar), 164.0 and 164.7 (carbons in the heterocycle), and 167.0 (C=O); [Found: C, 73.40; H, 6.35; N, 7.50; $C_{23}H_{24}O_3N_2$ requires C, 73.4, H, 6.4, N 7.4 %]. *m/z* (EI) 376

(80), 361 (100%), 161(40), 69(40) and 41(65) [Found: (M^+) 376.1787. $C_{23}H_{24}O_3N_2$ requires *M*, 376.17868].

Example 2:

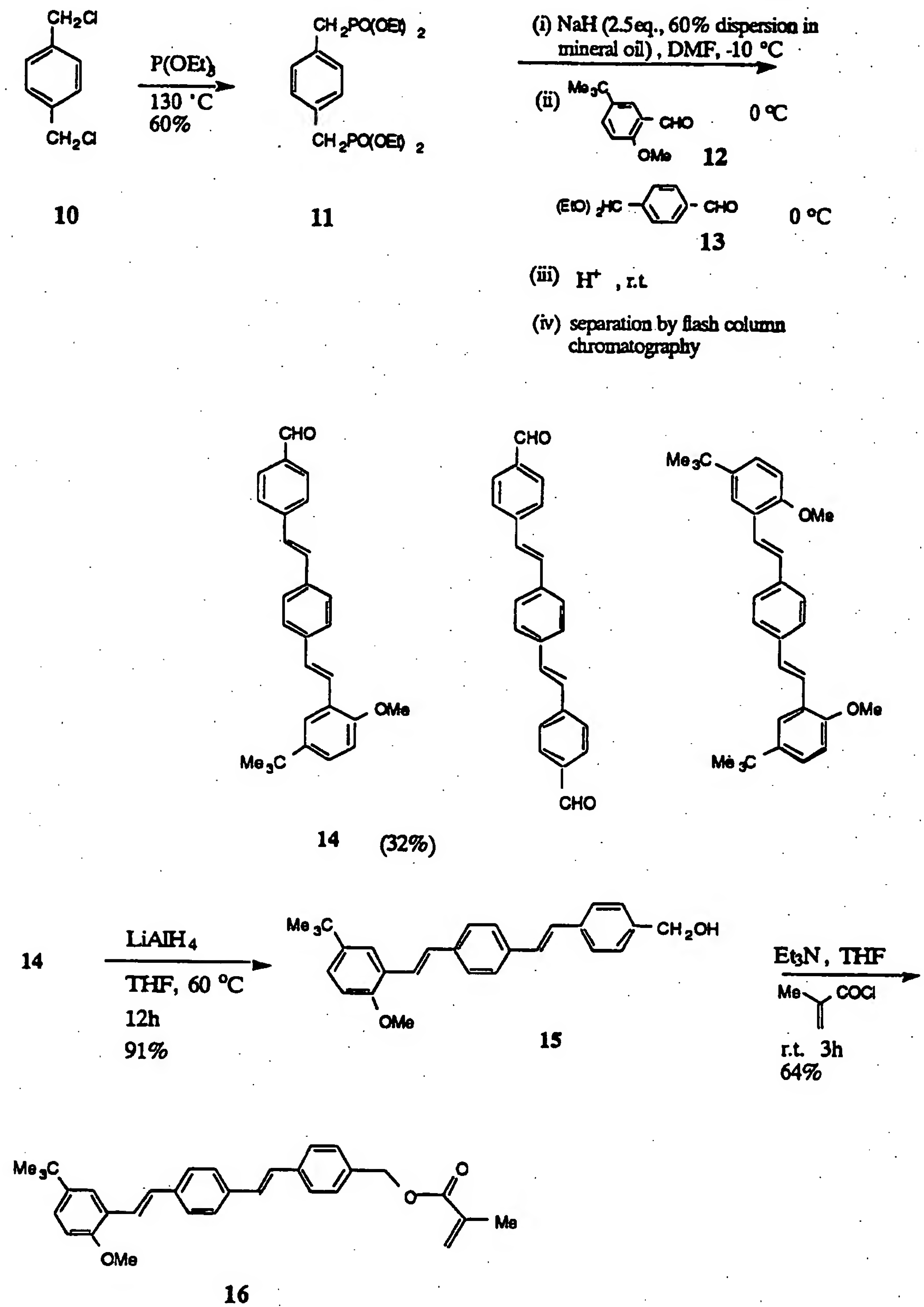
The Synthesis of Methacrylate Monomer PBD (9b):

Synthesis of 1-(4-phenyl-benzoyl)-2-(4-acetyloxyl-methyl-benzoyl)-hydrazine (6b): The synthesis is similar to that of (6a) except hydrazide (5b) was used instead of hydrazide (5a). After isolating the clay-like solid, it was recrystalised in 95% ethanol and dried at 100 °C under vacuum to give white crystals (6b) (88%). R_f 0.28 (ether); δ_H (250 MHz, $CDCl_3$) 2.13 (3 H, s, CH_3), 5.15(2 H, s, CH_2), 7.44 (5 H, m, Ar-*H*), 7.65, 7.92 (8 H, m, Ar-*H*); δ_C (63.5 MHz, $CDCl_3$) 20.9 (CH_3), 65.4 (CH_2), 127.2, 127.8, 128.0, 129.0, 130.0,131.0 (Ar), 139.8 (Ar-Ph_2), 140.5 (CC=O), 145.1 (CCH_2), 164.7(C=O), 170.7 (C=O). ν_{max} (chloroform)/cm^{-1}: 3407, 3234(N-H), 3013(C-H), 1736(CO-O), 1635, 1448(Ar), 965 (oxadiazole). [Found C, 69.8; H, 5.1; N, 7.0; $C_{25}H_{20}N_2O_3$ requires C, 71.11; H, 5.19; N, 7.21%].

Synthesis of 2-(biphenyl)-5-(4-acetyloxy-methyl-phenyl)-1,3,4-oxadiazole (7b): The cyclodehydration of **(6b)** to form **(7b)** is similar to the preparation of **(7a)**. Thus, **(6b)** (11.95 g, 30.76 mmol) was dissolved in $POCl_3$(40 ml). After refluxing for 6h, $POCl_3$ was removed by distillation before pouring the residue into ice water to obtain a light grey powder which was then washed with water(5 x 200 ml) until neutral. The crude product was purified by flash column chromatography using hexane-ether(1:1, v/v). (7b) was obtained as colourless crystals(5.57g, 40%). m.p.130-132 °C; R_f 0.71(ether); δ_H (250 MHz, $CDCl_3$) 2.16(3 H, s, CH_3), 5.20(2 H, s, CH_2), 7.50, 7.72 and 8.22(13 H, m, Ar-H); δ_C (63.5 MHz, $CDCl_3$) 20.9 (CH_3CO), 65.5(CH2), 122.6, 123.7(C-oxadiazole), 127.1, 127.3, 127.4, 127.7, 128.2, 128.6, 129.0 (Ar), 139.8, 144.6 (C-Ph), 164.3, 164.6(oxadiazole), 170.7 (C=O); ν_{max}(chloroform)/cm^{-1}: 3013(C-H), 1737(CO-O), 1614, 1550, 1484(Ar), 965(oxadiazole). [Found C, 74.76; H, 4.75; N, 7.54; $C_{23}H_{18}N_2O_3$ requires C, 74.58; H, 4.90; N, 7.56%].

<u>Synthesis of 2-biphenyl-5-(4-hydroxyl-methyl-phenyl)-1,3,4-oxadiazole (8b):</u> (7b) (7.0 g, 18.9 mmol) and sodium hydroxide(1.33g, 33.3 mmol) were dissolved in ethanol(95%, 350 ml) and stirred at room temperature for 3h before pouring the reaction mixture into sodium carbonate solution(600 ml) to obtain a white precipitate. The product was then dissolved in ethyl acetate, washed with water(3x300 ml) and dried with anhydrous sodium sulfate. The solvent was evaporated off and drying *in vacuo* yielded (8b) as fine white crystals (5.6 g, 90%). m.p.168-171 °C; R_f 0.71 (ether); δ_H (250 MHz, $CDCl_3$) 2.25(1 H, br, OH), 4.81(2 H, s, CH_2), 7.48(5 H, m, Ar-H), 7.70(4 H, m, Ar-H) and 8.15(4 H, m, Ar-H); δ_C (63.5 MHz, $CDCl_3$) 64.7 (CH_2), 122.7, 123.1 (C-oxadiazole), 127.2, 127.4, 127.7 128.2, 129.0 (Ar), 139.8, 144.5 and 144.9 (C-Ph, CCH_2), 164.5 (oxadiazole); ν_{max} ($CHCl_3$)/cm^{-1}: 3692, 3610(OH), 3015(H bonded OH), 1614, 1551 1484(Ar), 965(oxadiazole). [Found: C, 76.87; H, 4.75; N, 8.27. $C_{21}H_{14}N_2O_2$ requires C, 76.81; H, 4.91; N, 8.54%].

<u>Synthesis of methacrylate PBD monomer (9b)</u>: (8b) (3.86 g, 11.76 mmol) was dissolved in dry THF(150 ml) and dry triethylamine(12 ml, 0.49 mol), and stirred at 0 °C. Methacryloyl chloride(3 ml, 0.28 mol) was then added dropwise with a syringe. After stirring for 2h and then, warming up to room temperature, the cloudy solution was poured into ice water(600 ml) to get a white precipitate which was washed with water (5x150 ml) and then, dried to obtain the monomer (9b). TLC showed mainly one spot. R_f 0.38 (1:1 44ether-hexane v/v). The crude monomer was then further purified with flash column chromatography using ether-hexane. (9b) was obtained as white crystals(3.78 g, 81%). m.p.123-125 °C (possible polymerisation). δ_H (250 MHz, $CDCl_3$) 2.01(3 H, s, CH_3), 5.29(2 H, s, CH_2), 5.64(1H, s, CH=C), 6.21(1H, s, CH=C), 7.50(5 H, m, Ar-*H*), 7.72(4 H, m, Ar-H) and 8.22(4 H, m, Ar-H). δ_C (63.5 MHz, $CDCl_3$) 18.4 (CH_3), 65.7 (CH_2), 122.7, 123.7(*C*-oxadiazole), 126.2, 136.0 (*C*=C), 140.0, 144.6, 127.2, 127.4, 127.7, 128.2, 128.4, 129.0 (Ar), 164.3 and 164.6 (oxadiazole), 167.1 (*C*=O); ν_{max}($CHCl_3$)/cm^{-1}: 3012(C-H), 1717(CO-O), 1614, 1550, 1483 (Ar), 965 oxadiazole). [Found: C, 75.5; H, 4.9; N, 6.9. $C_{25}H_{20}N_2O_3$ requires C, 75.74; H, 5.08; N, 7.07%].



Scheme 7: Synthesis of methacrylate monomer (16)

Example 3:
The synthesis of methacrylate monomer TPV (16)

Synthesis of the alcohol (15)

To a solution of the bis-phosphonate (11) (3.3 g, 8.73 mmol) in DMF (30 ml), cooled to $0^{o}C$, was added sodium hydride (1.0 g, 25.0 mmol, 60% dispersion in mineral oil). The reaction mixture was stirred for 15 minutes. The substituted benzaldehyde (12) (1.75 g, 9.1 mmol) and terepthalaldehyde mono(diethyl) acetal (12) (2 ml, 10.05 mmol) in DMF (10 ml) was then added from a dropping funnel and the reaction mixture was then stirred for 2h at 0 °C in a cooling bath. HCl (3M, 10 ml) was added drop-by-drop to the cooled reaction mixture in order to destroy excess NaH and remove the acetal protecting group. The acidified mixture was stirred for 2h at room temperature and then poured into a large excess of distilled water. The crude mixture of products (yellow solids) were filtered out under suction and dried *in vacuo*. TLC(CH_2Cl_2) indicated three different compounds in the mixture of products. These compounds were separated by flash column chromatography (CH_2Cl_2). The desired aldehyde (14) was obtained (1.11 g, 32.1%).

The aldehyde (14) (1.1 g, 2.78 mmol) was dissolved in THF (30 ml) and cooled to 0 °C. $LiAlH_4$ (0.2 g, 5.0 mmol) was added slowly in two portions. The mixture was then refluxed overnight at 60 °C. Dilute acid (1M, 100 ml) was added, drop-by-drop to the cooled reaction mixture, to destroy excess $LiAlH_4$ and dissolve the alumina sludge formed. The aqueous mixture was extracted with CH_2Cl_2 (3x50 ml). The three CH_2Cl_2 portions were combined, washed with brine (50 ml), dried with anhydrous sodium sulfate and CH_2Cl_2 was evaporated off to yield the crude alcohol (15). The product was purified by flash column chromatography (eluting with 1:1 CH_2Cl_2-hexane to CH_2Cl_2 v/v) and was obtained as a yellowish-green solid (1.01 g, 2.54 mmol, 91%). [Overall yield : 29.1%]; R_f 0.53 (CH_2Cl_2); ν_{max} (KBr)/cm^{-1} 3386 (OH), 1493 (C=C), 1456 (C=C), 1362 (Ar), 1248 (C-O); δ_H (400 MHz, $CDCl_3$) 1.34 (9 H, s, *t*-Bu), 3.87 (3 H, s, OCH_3), 4.70 (2 H, d, *J* 4.6, CH_2), 6.84 (1 H, d, *J* 8.5, C=C*H*), 7.05-7.15 (3 H, m, *J* 9.4 and 6.4, C=C*H*), 7.27

(1 H, d, *J* 2.5, Ar-*H*), 7.36 (2 H, d, *J* 8.1, Ar-*H*), 7.46-7.55 (7 H, m, Ar-*H*), 7.59 (1 H, d, *J* 2.5, Ar-*H*)

Synthesis of methacrylate ester (16)

To a solution of alcohol (15) (1.01 g, 2.54 mmol) and triethylamine (0.6 ml, 4.3 mmol) in dry CH_2Cl_2 (20 ml), was added methacryloyl chloride (0.4 ml, 4.09 mmol). The mixture was stirred at room temperature for 3h. TLC(CH_2Cl_2) showed no presence of starting material (15). CH_2Cl_2 (80 ml) was added to the reaction mixture which was then washed with Na_2CO_3(50 ml), HCl (1M, 50 ml) and brine (50 ml). The aqueous portions were extracted with a further portion of CH_2Cl_2 (50 ml). The two CH_2Cl_2 portions were combined, dried with anhydrous magnesium sulfate and CH_2Cl_2 was evaporated off to yield the crude ester (16). The product was purified using flash column chromatography (eluting with 1:6 CH_2Cl_2-hexane followed by 1:4 CH_2Cl_2-hexane v/v). The ester was obtained as a green solid which luminescences blue under uv radiation (0.76 g, 1.63 mmol, 64.2%). R_f 0.13 (1:9 ether-hexane v/v); ν_{max} (KBr)/cm^{-1} 1716 (C=O), 1638 (C=C), 1603 (C=C), 1515 (Ar), 1494 (Ar), 1462 (Ar), 1156 (C-O); δ_H (400 MHz, $CDCl_3$) 1.34 (9 H, s, *t*-Bu), 1.97 (3 H, s, CH_3), 3.88 (3 H, s, OCH_3), 5.19 (2 H, s, CH_2), 5.59 (1 H, s, C=C*H*), 6.16 (1 H, s, C=C*H*), 6.84 (1 H, d, *J* 8.6, C=C*H*), 7.05-7.14 (3 H, m, *J* 11.0 and 5.2, C=C*H*), 7.28 (1 H, d, *J* 2.4, Ar-*H*), 7.36 (2 H, d, *J* 8.1, Ar-*H*), 7.46-7.56 (7 H, m, Ar-*H*), 7.60 (1 H, d, *J* 2.4, Ar-*H*); δ_C(100 MHz, $CDCl_3$) 167.29 (CO_2), 154.94 (C), 143.34 (C), 137.71 (C), 137.44 (C), 136.17 (C), 135.34 (C), 128.91 (C), 128.53 (C), 128.40 (C), 127.71 (C), 126.89 (C), 126.83 (C), 126.61 (CH), 125.85 (CH), 125.64 (C), 124.19 (CH) 123.55 (CH), 110.65 (CH), 66.22 (CO_2CH_2Ar), 55.65 (OCH_3), 34.19 (CMe_3), 31.56 ($C(CH_3)_3$), 18.37 (CH_3)

Example 4:

The polymerisation of methacrylate PPD monomer by anionic polymerisation (PMA-PPD-1)

<u>Preparation of (2,6-di-tert-butyl-4-methylphenoxy) diisobutylaluminium [Al(BHT)$^{i}Bu_2$]:</u> Di-*tert*-butyl-4-methylphenol (4.412 g, 20.0 mmol) was dissolved in toluene (20 ml). Triisobutyl aluminium (20 ml, 1M in toluene) was added by syringe, under N_2. The temperature was allowed to rise to 50 °C while butane gas was evolved. The mixture was then stirred at 50 °C for 1h. The flask was sealed with a septum and the mixture used as a stock solution.

The polymerisation:

n-Butyl lithium (0.05 ml, 15%) and Al(BHT)Bu_2 (1.5 ml) were dissolved in toluene (2 ml) and stirred under nitrogen for 30 mins at 0 °C. A solution of the monomer (14) (0.33 g, 0.9 mmol) in toluene (2 ml) was at first slowly added dropwise and a yellow colour formed. The monomer was then run in more quickly. After 2h, the colour had disappeared and the reaction appeared to have stopped. More BuLi (0.05 ml, 15%) was then added. After a further 3h, no polymer was observed by TLC. The reaction was therefore terminated by adding methanol. CH_2Cl_2 (200 ml) and water (100 ml) were added and the polymer was found at the bottom of the flask. The polymer was then extracted with excess $CHCl_3$. The solvent was removed under reduced pressure and the resulting polymer dissolved in the minimum amount of $CHCl_3$, filtered through a sand filled pipette and added to MeOH(200 ml). The resulting white polymer was collected by filtration giving polymer (15) (*ca.* 50 mg), m.p. 190-230 °C; ν_{max}(KBr)/cm^{-1} 2961, 1734 s (C=O), 1617, 1495, 1138, 1067 and 842; δ_H (250 MHz, $CDCl_3$) 1.24 (12 H, bs, α-CH_3 and C(CH_3)$_3$ group), 1.77 (2 H, b, CH_2), 5.29 (2 H, s, CH_2), 7.37 and 7.88 (2 x 4H, b, Ar-*H*); δ_C (63.5 MHz, $CDCl_3$) 31.0 (CH_3 and C(CH_3)$_3$), 35.0(*C*(CH_3)$_3$), 44.9 (CH_2), 66.1 (CH_2-OH), 120.8, 123.8, 125.9, 126.6, 126.9, 129 1, 138.4, 155.2, 163.6 and 164.5 (Ar) and 176.5 (*C*=O). [Found: C, 64.6; H, 5.9;

N, 6.3; $C_{23}H_{24}O_3N_2$ requires: C, 73.4; H, 7.4; N, 7.4%]; GPC assay revealed ($CHCl_3$, polystyrene as standard): M_n =36,000, M_w =489,000.

Example 5:

Polymerisation of methacrylate PPD monomer (9a) by radical polymerisation (PMA-PPD-2): Monomer (9a)(0.33 g, 0.89 mmol) was dissolved in AIBN solution in benzene (5 ml, 0.3 mg, 1.83 x 10^{-6}mol). The ratio of AIBN/monomer is 0.21% (mol/mol). After removing ca. 4ml of benzene *in vacuo*, the solution was thoroughly degassed by several freeze-thaw-pump cycles (five to eight times). The reaction mixture was stirred at 80 °C for 2h before cooling down to room temperature. The viscous reaction mixture was poured into MeOH (10 ml) to obtain a white precipitate which was then, washed with MeOH(3x2 ml) and dried to yield crude polymer (9a)(0.22 g, 69%). The polymer was further purified by dissolving in chloroform and reprecipitation in MeOH (repeated 3 times). δ_C (250 MHz, $CDCl_3$) 0.67, 0.98(3H, b, α-CH_3), 1.24(9 H, $C(CH_3)_3$), 1.87(2H, CH_2), 4.87(2H, b, CH_2), 7.37, 7.88(2x4 H, Ar-*H*); δ_C(100 MHz, $CDCl_3$) 16.9, 19.0(a-CH_3), 31.0($C(CH_3)_3$), 35.0(CMe_3), 45.0(CH_2), 54.1(CC=O), 66.1(CH_2OCO), 120.8, 123.8, 125.9, 126.7, 126.9, 129.1, 138.5, 155.2(Ar), 163.7, 164.5(oxadiazole), 176.8(*C*=O); ν_{max} ($CHCl_3$)/cm^{-1}: 2966(C-H), 1728(C=O), 1615, 1552, 1494(Ar), 964(oxadiazole); [Found: C, 72.69; H, 6.30; N, 7.22; $C_{23}H_{24}N_2O_3$ requires: C, 73.38; H, 6.43; N, 7.44%]; GPC assay revealed ($CHCl_3$, polystyrene as standard) M_n=52,000, M_w=127,000, M_w/M_n=2.46.

Example 6:

The polymerisation of mathacrylate PPD monomer (9a) by radical polymerisation method (PMA-PPD-3)

The polymerisation procedure is similar to Example 5 except

AIBN was used as initiator (0.5% by mol with respect to amount of monomer). After purification by dissolving in $CHCl_3$ followed by precipitation into MeOH (repeated three times), polymer (9a) was obtained (55%). GPC assay revealed ($CHCl_3$, polystyrene as standard): M_n=34,000, M_w=103,000, M_w/M_n=2.99.

Example 7:

Polymerisation of methacrylate PBD (9b) (PMA-PBD-1):

The polymerisation of monomer (9b) is similar to that of (9a) in Example 5. Thus, monomer (9b) (0.35 g of, 0.885 mmol) was dissolved in a benzene solution containing AIBN (5.4 ml, 0.73 mg AIBN) (AIBN/monomer=0.5%, by mol). Excess benzene was evaporated of *in vacuo* until ca. 0.5 ml to 1.0 ml of benzene remained in the reaction mixture. The solution was then completely degassed using several freeze-thaw-pump cycles (five to eight times). The reaction mixture was stirred at 80 °C under a N_2 atmosphere, for 2h. On cooling to room temperature, the viscous reaction mixture was poured into methanol-acetone (20 ml, 1:1 v/v) to obtain a white precipitate. The polymer was then purified by repeatedly dissolving in $CHCl_3$ and precipitating into methanol-acetone (repeated 3 times). After drying *in vacuo*, (9b) was obtained as a white powdery solid (0.23 g, 66%). δ_H (250 MHz, in $CDCl_3$) 0.66-0.98 (3 H, b, a-CH_3), 1.90 (2 H, b, CH_2), 4.86 (2H, b, CH_2), 7.28, 7.47 (9 H, b, Ar-*H*), 7.85 (4 H, b, Ar-*H*); δ_C (100 MHz, $CDCl_3$) 18.5 (CH_3), 29.5 (CH_3), 44.9 (CH_2), 65.7 (CH_2), 122.7, 123.7 (Ar-oxadiazole), 126.9, 127.2, 127.4, 127.7, 128.1, 128.4, 128.8 and 129.0 (Ar), 139.4, 144.5 (Ar-Ph, Ar-CH_2O), 163.8 (C, oxadiazole), 164.2 (C, oxadiazole); ν_{max} (KBr)/cm^{-1}: 3010 (C-H), 1730 (CO-O), 1614, 1550, 1484 (Ar), 964 (oxadiazole); [Found: C, 74.44; H, 4.92; N, 6.66; $C_{25}H_{20}N_2O_3$ requires: C, 75.74; H, 5.08; N, 7.07%]; GPC assay revealed ($CHCl_3$, polystyrene as standard): M_n=89,000, M_w=103,000.

Example 8:

The polymerisation of mathacrylate monomer PBD (9b) (PMA-PBD-2):

The polymerisation procedure is similar to Example 7 except chlorobenzene rather than benzene, was used as solvent. The polymer was then purified by repeatedly dissolving in $CHCl_3$ and precipitating into methanol-acetone (repeated three times). (9b) was obtained in 50% yield. GPC assay revealed ($CHCl_3$, polystyrene as standard): M_n=4,080, M_w=42,500.

Example 9:

The polymerisation of methacrylate TPV (16) (PMA-TPV):

The polymerisation of monomer (16) is quite similar to that of monomer (9). Thus, monomer (16) (0.205 g, 0.44 mmol) was dissolved in benzene solution (2.5 ml) containing 0.35 mg of AIBN (10.8 mg, 0.85 mmol). The solution was then concentrated by evaporating off some benzene *in vacuo* and then thoroughly degassed by using the freeze-thaw-pump method (repeated five times). The reaction mixture was then stirred at 80 °C for 2h under an inert nitrogen atmosphere. The homopolymer was precipitated out in excess methanol and purified by dissolving in $CHCl_3$ and reprecipitation in excess MeOH (repeated twice). The polymer was dried overnight *in vacuo* and was obtained as a pale yellow powdery solid (0.11 g, 54%). ν_{max} (KBr)/cm^{-1} 1720 (C=O), 1613 (C=C), 1514 (Ar), 1465 (Ar), 1150 (C-O); δ_H (400 MHz, $CDCl_3$) 0.5-1.1 (b, backbone α-Me), 1.1-1.25 (b, backbone CH_2), 1.29 (9 H, s, $C(CH_3)_3$), 3.74 (3 H, s, OCH_3), 4.6-5.2 (2 H, b, CO_2CH_2), 6.7-7.1 (2 H, b, CH=C*H*), 7.1-7.7 (13 H, b, CH=C*H* and Ar-H); l_{max}/nm ($CHCl_3$): 245, 324; GPC assay revealed ($CHCl_3$, polystyrene as standard) M_n = 161,000, Mw=702,000, M_w/M_n= 4.37.

Example 10:

'Screened' anionic polymerisation of methyl methacrylate.
of methacrylate monomer TPV (16) by anionic polymerisation:

10.1 Preparation of 2,6-di-tert-butyl-4-methylphenoxy) diisobutylaluminium [$Al(BHT)^{i}Bu_2$]

Di-*tert*-butyl-4-methylphenol (4.412 g, 20.0 mmol) was dissolved in toluene (20 ml). Triisobutyl aluminium (20 ml, 1M in toluene) was added by syringe, under N_2. The temperature was allowed to rise to 50°C. Butane gas was evolved. The mixture was then stirred at 50°C for 1 h. The flask was sealed with a septum and the mixture was used as a stock solution.

10.2. Polymerisation of methyl methacrylate

A solution of $Al(BHT)^{i}Bu_2$ (3 ml, 1.5 mmol, 0.5M in toluene) was mixed with toluene (15 ml) in a 3 neck 100 ml RB flask fitted with a presure equalising dropping funnel, N_2 balloon and a spetum. *tert*-Butyllithium (0.3 ml, 1.7M in pentane) was then added by syringe, with stirring. Several minutes were allowed to elapse to permit complete complexation ofthe two metal alkyls. Methyl methacrylate (MMA) (2ml, 1.87 g, 18.7 mmol) was added drop-by-drop from the dropping funnel. The mixture was stirred at 0°C for 1 h. The addition of MMA produced a pronounced yellow colour in the solution but on completion of the polymerisation, the solution is colourless. The polymer was precipated out in excess hexane and dried *in vaccuo* overnight. Yield (1.7 g, 90%); m.p. 173-280°C; $\nu_{max}(KBr)/cm^{-1}$ (1731 (C=O), 1150 (C-O); δ_H(400 MH\, $CDCl_3$) 0.75-1.1 (b, 3H, α-CH_3), 1.7-2.1 (b, 2H, CH_2), 3.59 (s, 3H, CH_3); Tactility δ_H (triad, %); 0.83 (rr, 68.8%), 1.01 (mr, 31.2%). GPC in chloroform revealed M_n 25,980, M_w/M_n = 1.35.

Example 11:

The copolymerisation of methacrylate PBD and TPV:

The copolymerisation of monomer (9b) and monomer (16) was been carried out using radical copolymerisation method that is

similar to homopolymerisation. Thus, monomer (9b) (0.211 g., 0.532 mmol) and (16) (0.250 g, 0.537mmol) were first dissolved in a benzene solution(6.5 ml) that contain 0.8839 mg of AIBN (AIBN/(17+18)=0.5%, by mol) to form a homogeneously dispersed solution. The solution was then concentrated to ca. 1 ml by evaporating off some benzene *in vacuo* and then, completely degassed by using the freeze-thaw-pump method (repeated five times). The reaction mixture was stirred at 80 °C for 2h under an inert nitrogen atmosphere. After cooling down to room temperature, the viscous solution was poured into MeOH(20 ml) to obtain a white precipitate which was then further purified by repeatedly dissolving in chloroform and precipitating into methanol (repeated three times). The copolymer was obtained as a light yellow powdery solid(0.29 g, 63 %). δ_H(250 MHz, $CDCl_3$) 0.67-1.16(2 x 3H, b, 2 x a-CH_3), 1.33(9 H, s, ^{t}Bu), 1.61(4 H, CH_2), 3.88(3 H, OCH_3), 4.82(4 H, s, CH_2), 6.72-7.9(24 H, b, Ar-*H*); δ_C(100 MHz, $CDCl_3$) 31.5($C(CH_3)_3$), 34.1(CMe_3), 55.5(OCH_3), 110.5(*C*H=CH), 123.4, 124.0, 126.6, 127.0, 127.2, 127.4, 127.8, 128.2, 128.5, 129.0, 137.4(Ar); ν_{max}(KBr)/cm^{-1} 2949(C-H), 1724 (C=O), 1610, 1548(Ar), 961(oxadiazole); GPC assay revealed ($CHCl_3$, polystyrene as standard) M_n = 44,000, Mw=242,000, M_w/M_n5.45.

Example 12

Poly(methacrylate) PPD as single electron transporting layer:

In order to evaluate the applicability of the polymers in LED devices, two double layered LED devices have been fabricated using PPV as a hole transport layer and either aluminium or calcium as the negative electrode.

<u>LED device fabrication</u>: ITO glass was cleaned in an ultrasonic bath with detergent solution for 20 minutes and then rinsed with distilled water, acetone and isopropanol before drying in a stream of N_2. The dry and absolutely clean ITO glass substrate was then spin-coated with a PPV precursor solution(1% in methanol) at room temperature at 2000 rpm for 20 minutes. Thermal conversion of the PPV precursor was carried out at 280 °C *in*

vacuo (ca. 0.1 mmHg) for 4h to obtain a PPV layer(with thickness of ca. 40 nm). The PPV layer functions as both a hole-transport and light-emitting layer. The oxadiazole containing polymer PMA-PPD-2 (usually 2% in chloroform) was then spin-coated onto the converted PPV layer before depositing aluminium on the top to form the double layer LED device.The electrodes were led out using a copper adhesive tape strip and then covered with PVC adhesive tape to prevent contact with air.

(1) ITO/PPV/PMA-PPD/Al	No light emission bellow 28V
(2) ITO/PPV/PMA-PPD/Ca	Green yellow light emission

The above results show that when aluminium is used as the negative electrode, incorporation of a PMA-PPD layer in the double layer device has no apparent benefits. However, light emission(below 28V) is enhanced when calcium is used as the cathode. Fig. 1 shows that the internal quantum efficiency of the double layer device(2) can be increased by about four folds, while the turn-on voltage is apparently reduced (Fig. 2).

Example 13:

<u>Poly(methacrylate) (PPD) used as an electron transporting layer in the form of a blend, with stilbene containing poly(methacrylate) derivative (TPV)</u>:

Alternatively, PMA-PPD has been used in a blend with a blue light-emitting polymer (PMA-TPV), with PPV being used as a hole transporting layer, in a series of devices. These devices were fabricated using the similar procedure described in Example 12, except PMA-TPV(2% in chloroform), and a blend solution of PMA-TPV and PMA-PPD-2(1:1 w/w in chloroform) were used instead.

(3) ITO/PMA-TPV/Ca	No light emission
(4) ITO/PPV/PMA-TPV/Ca	No light emission
(5) ITO/PPV/Blend of PMA-TPV+ PMA-PPD/Ca	Blue light emission

and gradual change to green light emission

(6) ITO/PPV/PMA-TPV+PMA-PPD/Al No light emission

These results suggest that PMA-TPV does not electroluminese bellow 28V unless an electron transporting polymer PMA-PPD is also used (device 3). For device 4, blue light emission was initially observed but the colour gradually changed to green within 20 minutes on continuous charge application at a bias voltage of ca. 15V(as shown in Fig. 3). Fig. 4b shows that the internal quantum efficiency of the device increased after storing the device for a week.

Example 14:

<u>Poly(methacrylate) PBD as single electron transport layer:</u>

According to the LED fabrication procedure described in Example 12, PMA-PBD-1 solution in chloroform was spin-coated onto a PPV layer, on an ITO glass substrate, thus forming a LED device using PMA-PBD as the electron transporting layer:

(7) ITO/PPV/PMA-PBD/Ca. Green light emission

Green light emission was observed when a bias voltage of 15V was applied.

Example 15:

<u>Poly(methacrylate) PBD used as electron transport layer in the form of a blend with poly(methacrylate) TPV as the emitting polymer</u>:

A blend solution of PMA-PBD-1/PMA-TPV(1:1 w/w) in chloroform was used to spin-coat a film onto a layer of PPV, on an ITO glass substrate.

(8) ITO/PPV/PMA-PBD+PMA-TPV/Ca Blue light emission

Blue light emission was observed at a bias voltage of 20V in the first 30 minutes followed by a continuous green light emission(Fig. 5). The PMA-PBD polymer is used as an electron-transporting functional layer, while the PMA-TPV polymer was used to produce blue light emission. The PMA-TPV polymer also exhibits some cross-linking potential.

Example 16:

Poly(methacrylate) PBD-TPV copolymer used as a blue light emitting layer, in a double layer device:

In an series of LED devices, it has been found that incorporation of PMA-PBD showed no benefit in enhancing light-emission from a PPV or PMA-TPV layer, when aluminium was used as the cathode[devices (9) and (10)]. However, PBD segments in the copolymer PMA-TPV-PBD does enhance or aid blue light emission from the TPV chromophores in the copolymer[as shown in device (13)].

(9) ITO/PPV/Al No light emission
(10) ITO/PPV/PMA-PBD/Al No light emission
(11) ITO/PPV/PMA-TPV/Al No light emission
(12) ITO/PPV/Blend of PMA-TPV+PMA-PBD/Al Blue light emission but less stable
(13) ITO/PPV/Copolymer of PMA-TPV-PBD/Al Blue light emission

These results suggest that the use of electron transporting segments in the copolymer is better than that in the form of a blend [compare device (12) with (13) and (14)]. Fig. 6 shows that the turn-on voltage for the device is about 16V, and the light intensity will increase along with the increase of the applied voltage until 23V(device break-down occurs beyond that

voltage)(Fig.6). It can be seen from Fig.7, that the colour of the light emitted is blue since the peak maxima in the electroluminescence spectrum is located at 457nm. This is in the blue region of the visible spectrum. It can also be seen from Fig.8 (line 2), that there is light emission from the PPV layer since there are two electroluminescent shoulders at 554nm and 507nm, which are typical of PPV emission[Fig. 8 (line 3)]. The PPV emission is further confirmed when the colour of light emitted gradually changes from blue to green on continuous charge application. This suggest the break-down of the TPV chromophores in the PMA-TPV-PBD copolymer, thus leaving PPV as the sole light-emitting polymer. Fig.9 shows that the device has a fairly high internal quantum efficiency(with 0.035%) considering aluminium is used as the cathode.

Example 17:

Copolymer PMA-TPV-PBD used as a blue light emitting layer in a single layer device:

The copolymer solution(2 % in chloroform) was directly spin-coated onto a clean ITO glass substrate followed by the deposition of aluminium to form a single layer LED device:

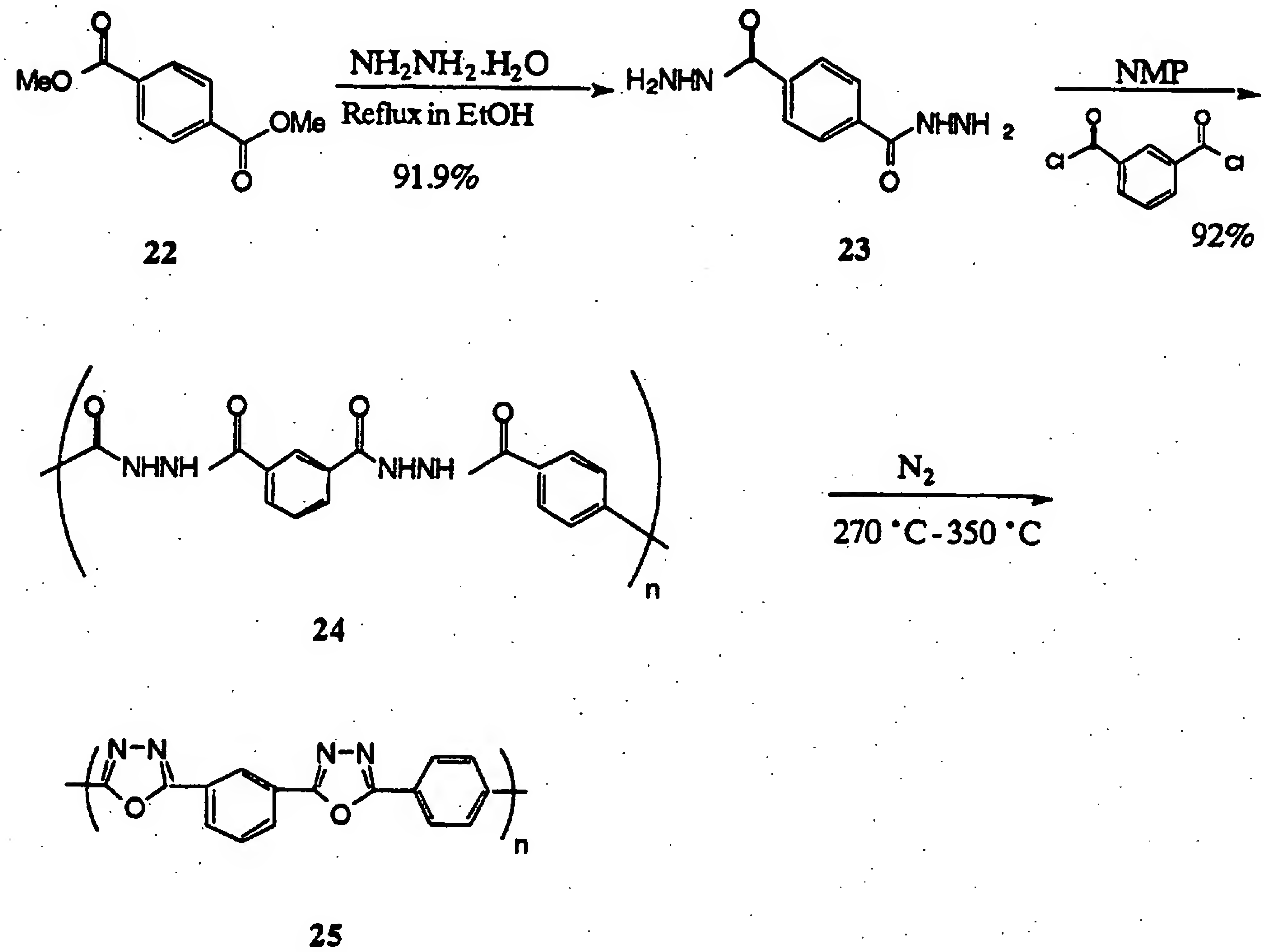
(14) ITO/PMA-TPV-PBD/Al   Blue light emission

Blue light emission was observed when a bias voltage(20V) was applied but the device appears to be less stable compared to the double layered LED device (13).

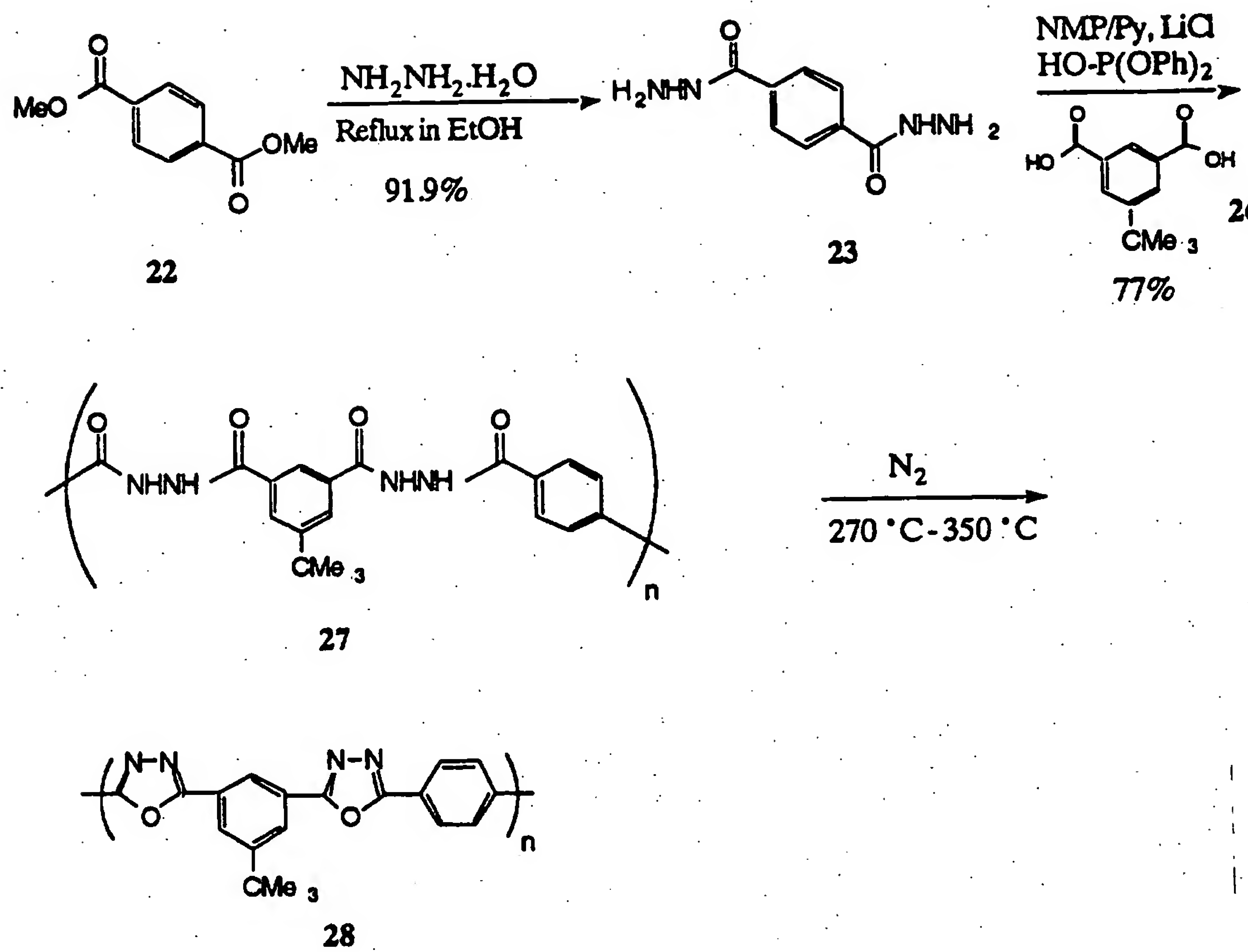
THE PREPARATION AND APPLICATION OF MAIN CHAIN LED POLYMERS THROUGH A PRECURSOR ROUTE

Poly(methacrylates) have many advantages such as high transparency, high resistance to chemicals and good mechanical

strength. High molecular weight poly(methacrylates) as well as multi-functional copolymers can also be easily obtained. However, poly(methacrylate) derivatives may not be good candidates for polymers which exhibit high stability and resistance to an electrical field. Therefore, they may have a life-time problem in applications involving LED devices. In order to prevent this problem, one approach involves the introduction of another chain segment which contains cross-linkable groups such as TPV. Another way to improve the resistance to an electrical field is to choose other types of polymer chains such as rigid-rod polymers or ladder polymers. However, there is a severe processability problem for rigid-rod or ladder polymers due to their low solubility in conventional organic solvents. The processability of these polymers can be improved by using a soluble precursor which can be converted to a rigid and conjugated polymer. Here, we have tried a precursor route for the synthesis of polyaromatic oxadiazoles as shown in Scheme 8 and Scheme 9.



Scheme 8 : Precursor route for the synthesis of an aromatic oxadiazole polymer



Scheme 9 : A Precursor route for the synthesis of a ^{t}Bu- aromatic oxadiazole polymer

EXAMPLE 18:

Synthesis of Polyaromatic hydrazide (24): 1,3-isophthaloyl dichloride(5.31 g, 26.17 mmol) was added to the slurry of (23) (5.08 g, 26.17 mmol) in N-methylpyrolidone(NMP) (50 ml) and LiCl (4.86 g) in a 250 ml, 3-neck RB flask. The reaction was stirred for 5h at 0 °C before pouring the viscous reaction mixture into

water to obtain a white precipitate which was then washed with 1% LiOH(aq) solution, water and methanol respectively. The polymer was purified by Soxhlet extraction using methanol(8h) and dried *in vacuo* at 110 °C for 8h. (24) was obtained as a white powdery solid(7.82 g, 92%). δ_H (200 MHz, DMSO-d_6) 7.73(1H, s), 8.15(2 H, d, Ar-*H*), 8.09(4 H, s), 8.52(1 H, s, Ar-*H*), 10.77(4H, s, 2xN*H*N*H*); δ_C (100MHz, DMSO-d_6) 127.2, 128.5, 130.0, 131.4, 133.0, 135.5(Ar), 165.3*C*=O), 165.5(*C*=O); ν_{max}(KBr)/cm^{-1} 3252(N-H), 1685(C=O), 1654(CO-NH), 1560, 1508, 1488 (Ar); Intrinsic visicosity: 0.5 dL/g (30 °C in DMSO).

EXAMPLE 19

Preparation of polyaromatic oxadiazole (25): The polyaromatic hydrazide (24) will be thermally converted to (25) at 270 °C(or above) under nitrogen or *in vacuo* for at least 24h. ν_{max}(KBr)/cm^{-1}: 1700(residue of CO-NH), 1609, 1543, 1478, 1458(Ar), 961(oxadiazole); $\lambda_{max/film}$: 227, 335nm.

EXAMPLE 20

Preparation of polyaromatic hydrazide-*tert*-Bu (27): A 250 ml 3-neck RB flask with a condensor, a mechanic stirrer and thermometer was charged with (23) (3.88 g, 0.02mol), 5-*tert*-butyl-1,3-isophthalic acid (26) (4.44 g, 0.02 mol), and LiCl (6.0g) dissolved in dry NMP(60 ml) and dry pyridine(40 ml). The reaction was carried out in the presence of diphenyl phosphite (14.05 g, 60 mmol) at 120 °C for 2.5h. The sticky, opaque solution was poured into methanol(500 ml) to obtain a white precipitate which was then washed with methanol(4x200 ml) and then, extracted using methanol in a Soxhlet apparatus for 20h. After drying *in vacuo*, (27) was obtained as a white solid (5.85 g, 77%). δ_H (200 MHz, DMSO-d_6) 1.43(9H, s, C(C*H*$_3$)$_3$), 8.10(4H, b), 8.20(2 H, b), 8.37(1H, Ar-*H*), 10.77, 10.80(4H, 2, 2xN*H*N*H*); σ_C(100MHz, DMSO-d_6) 31.0(C(*C*H$_3$)$_3$), 35.1(*C*Me$_3$), 122.1, 124.8, 127.9, 132.9, 135.6, 151.8(Ar), 165.3(*C*=O), 165.7(*C*=O); ν_{max}(KBr)/cm^{-1} 3252(CO-N-H), 2957(C-H), 1654(CO-NH), 1543, 1478(Ar); [Found: C, 60.60; H, 5.64; N, 14.47. $C_{20}H_{20}N_4O_4$ requires:

C, 63.13; H, 5.30; N, 14.47%].

EXAMPLE 21

Preparation of polyaromatic oxadiazole-*tert*-Bu (28): The polyaromatic hydrazide-^{t}Bu polymer (27) was thermally converted into polymer (28) under nitrogen or *in vacuo* at 270 °C(or above) for at least 24h. ν_{max}(KBr)/cm^{-1} 2957(C-H), 1543 s, 1482(Ar), 962(oxadiazole); [Found: C, 68.64; H, 4.65; N, 15.64. $C_{20}H_{16}N_4O_2$ requires: C, 68.54; H, 4.69; N, 16.28%].

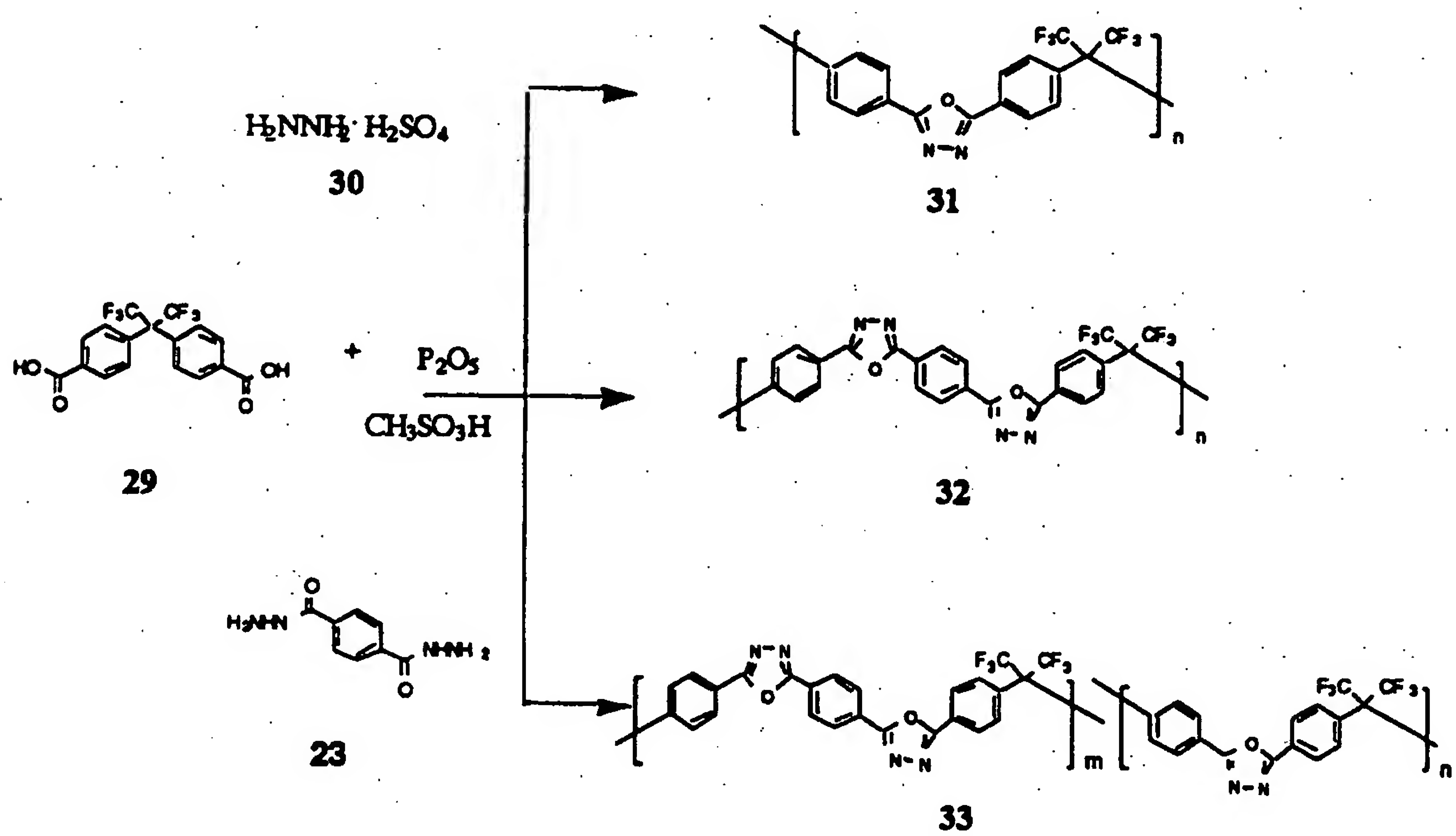
THE PREPARATION AND APPLICATION OF MAIN CHAIN POLYMERS THROUGH THE INTRODUCTION OF FLEXIBLE SPACERS

The introduction of a flexible spacer into a conjugated or rigid polymer chain will usually enhance the solubility of the polymer. The following examples illustrate the preparation and application of three different polymers with a hexafluopropylene spacer. (Scheme 10)

Example 22:

Preparation of Poly(phenylene-1,3,4-oxadiazole-2,5-diylphenylene-2,2-hexafluoropropylidene) (31): Phosphorus pentoxide (2.95 g, 20.0 mmol) was dissolved in methanesulfonic acid (20 ml) upon stirring at 80 °C over 30 min. Hydrazine sulfate (1.302 g, 10.0 mmol) and 2,2-bis(4-carboxyphenyl)hexafluoropropane (29) (3.923 g, 10.0 mmol) were added and the mixture stirred for 24h at 80 °C. The solids dissolved slowly within 30 min. On cooling to room temperature, the yellow viscous solution was poured into water (300 ml) and neutralised with saturated aqueous Na_2CO_3 (40 ml). The precipitate(fibre-like) was filtered out under suction and washed with water (3x300 ml), and finally purified by dissolving in chloroform and precipitating out in methanol(repeated three times). (31) was obtained as grey-white fibres which

melted/decomposed above 270 °C(2.79 g, 75.4%). λ_{max}(chloroform) 300nm; λ_{max} (solid film) 290nm; ν_{max} (KBr)/cm^{-1} 1618, 1585, 1551, 1499, 1420, 1256, 1210, 1175, 1140, 1071 10120, 971, 928, 840 723; δ_H (400 MHz, $CDCl_3$) 7.60-8.18 (8H, b, Ar-*H*); δ_C (100 MHz, $CDCl_3$) 122.3, 124.8 , 125.3(*ipso*-C), 127.1 and 131.0 (CH), 136.5(*ipso*-C); [Found: C, 54.99; H, 2.29; N, 7.56. $C_{17}H_8F_6N_2O$ requires: C, 55.15; H, 2.18; N, 7.57%]; The polymer was insoluble in ethyl acetate, ether, acetonitrile, toluene and acetone but soluble in tetrahydrofuran, dichloromethane and chloroform. GPC assay revealed ($CHCl_3$, polystyrene as standard, 10 ml/min flow rate) M_n = 11,800, Mw=143,000, M_w/M_n= 12.



Scheme 10: The synthesis of fluorine-containing polyaromatic oxadiazoles

EXAMPLE 23

The preparation of polymer (32):

The synthesis procedure for polymer (32) is quite similar to

that of polymer (31). Phosphorus pentoxide (2.70 g) was dissolved in methanesulfonic acid (16.0 ml) upon stirring at 80 °C over 30 min. Hydrazide (23) (1.6355 g, 8.42 mmol) and 2,2-bis(4-carboxyphenyl) hexafluoropropane (29) (3.301 g, 8.42 mmol) were added and the mixture stirred for 24h at 80°C. After the mixture was cooled to room temperature, the yellow viscous solution was poured into water (300 ml) and neutralised with saturated aqueous Na_2CO_3 (40 ml). The precipitate was filtered out under suction and washed with water (3x300 ml), and finally purified by Soxhlet extraction with methanol for 48h. (32) was obtained as a grey powdery solid which melted/decomposed above 270 °C (3.43 g, 79.2 %). λ_{max} (solid film) 312nm. ν_{max} (KBr)/cm^{-1} 1725, 1617, 1576, 1552, 1497, 1415, 1327, 1256, 1210, 1174, 1140, 1072, 1017s, 970, 928, 838, 722; δ_H (400 MHz, $CDCl_3$) 7.43(4H, s, Ar-*H*), 7.64(4H, s, Ar-*H*), 7.85(4H, s, Ar-*H*); δ_C (100. MHz, $CDCl_3$) 123.8, 124.3 , 127.2, 127.8, 129.8, 130.8, 133.0, 133.8, 141.6.

EXAMPLE 24

The preparation of Polymer (33)

The synthesis procedure of polymer (33) is quite similar to that of polymer (31). Phosphorus pentoxide (1.860g) was dissolved in methanesulfonic acid (12.0 ml) upon stirring at 80 °C over 30 min. Hydrazide (23) (0.611 g, 3.148 mmol), hydrazine sulfate(0.410 g, 3.148 mmol) and 2,2-bis(4-carboxyphenyl)hexafluoropropane (29) (2.47 g, 6.30 mmol) were added and the mixture stirred for 24h at 80 °C. After the mixture had cooled down to room temperature, the yellow viscous solution was poured into water (300 ml) and neutralised with saturated aqueous Na_2CO_3 (40 ml). The precipitate was collected by suction filtration and washed with water (3x300 ml), and finally purified by Soxhlet extraction with methanol for 48h. (33) was obtained as a grey powdery solid which melted/decomposed above 270 °C(2.54 g, 91.4 %). λ_{max} (solid film) 320nm. δ_H (250 MHz, $CDCl_3$) 7.41(4H, s, Ar-*H*), 7.90(4H, s, Ar-*H*), 8.13(2H, s, Ar-*H*); δ_C (100 MHz, $CDCl_3$) 124.2, 124.4 , 125.0, 127.8, 128.5(C), 130.4, 131.5, 134.5(CH), 142.3(C).

EXAMPLE 25

Polymer (31) as a single electron transport layer

Clear polymer (31) solution(1% in chloroform, filtrated through 0.45 μl membrane) was spin-coated onto a PPV layer(ca. 40 nm thickness on an ITO glass substrate). Aluminium was then evaporated on top of the film of polymer (31)(ca. 40 nm) to form a double layer polymer LED device [ITO/PPV/P-31/Al]. A more stable green light emission was obtained at a bias voltage of 22V, in comparision to a device without P-31.

EXAMPLE 26

Polymer (31) as electron transporting polymer in a blend form with polyalkylthiophene

A clear blend of polymer solution(1 % in chloroform, filtrated through 0.45 ul membrane) [1:1 ratio of polymer-(31):poly[3-(2-dimethyl ethyl) thiophene)] was spin-coated onto a dry and clean ITO glass substrate. Aluminium was then evaporated on top of the film of polymer blend (ca. 40 nm) to form a double layer polymer LED device: [ITO/PAT+P-31/Al]. A more stable yellow light emission was obtained at a bias voltage of 18V, in comparision to a device without P-31.

EXAMPLE 27

Polymer (32) as both an electron transporting polymer and electroluminescent polymer in a double layer device

A clear solution of polymer (32)(1% in trifluoroacetic acid, filtered through 0.6 ul pore size membrane) was spin-coated onto a PPV layer(ca. 40 nm thickness on an ITO glass substrate). Aluminium was then evaporated on top of the film of polymer (32)(ca. 40 nm) to form a double layer polymer LED device: [ITO/PPV/P-32/Al]. Green light emission was observed at a bias voltage of 15V, which then turned to blue purple when a higher bias voltage(28V) was applied.

The Synthesis of Polythiophenes 45a-c

The synthesis of the relevant polythiophenes **45a-c** is shown in Scheme 11

The relevant thiophene monomers **1** and **2** have been reported (K.A. Murray, S.C. Moratti, D.R. Baigent, N.C. Greenham, K. Pichler, A.B. Holmes and R.H. Friend, *Synth. Met.*, 1995, 69, 395-396).

The regioregular polythiophenes chosen to illustrate crosslinkable polymers are poly(3-hexylthiophene)s containing a small amount of 11-hydroxyundecyl side chains. The monomers have been copolymerised in ratios of 19:1 **1**:**2** up to 2:1 **1**:**2**, to give the tetrahydropyranyl acetal protected copolymers **43**. These can be deprotected to give the alcohol-functionalised copolymers **44** (scheme 11). Conversion to the azide is achieved in one step using excess diphenylphosphoryl azide and has been carried out on 19:1, 9:1 and 4:1 ratio copolymers **44** to give azidated copolymers **45a**, **45b** and **45c** respectively; no residual alcohol can be seen by ^1H NMR.

Thermal decomposition of the azide was achieved by heating films of polymers **45a-c** to 200 °C under vacuum for 30 minutes; differential scanning calorimetry of polymer **45b** indicates that azide decomposition occurs above 185 °C. Azide decomposition results in loss of nitrogen and the formation of a highly reactive nitrene which is expected to react fairly indisciminately with single and double bonds. A change in the UV-visible absorption spectra of the polymers is observed on crosslinking; the spectrum shifts to lower wavelength (higher energy) possibly due to a shorter conjugation length due to nitrene insertion along the polymer backbone and this effect increases with the azide content of the polymer (Figure 11, Table 1). The resulting films were washed with chloroform and were insoluble but showed a slight colour change (Table 1). A small amount of soluble, non-crosslinked polymer was washed from the 19:1 copolymer (ex **45a**) but the remaining polymer was fully insoluble.

Polymer	Ratio hexyl: azide	λ_{max}/nm before heat	λ_{max}/nm after heat	λ_{max}\nm $CHCl_3$ washed	λ_{max}/nm in chloroform
45a	19:1	520	510	502	458
45b	9:1	522	496	488	458
45c	4:1	522	486	482	462

Table 1 : Thermal crosslinking of regioregular polythiophenes with different azide contents.

The resultant insoluble polythiophene films can be used in device formation, as further layers might be spun from solution on top of the polythiophene without causing any damage. It is also possible that physical properties could be tailored by altering the azide concentration and controlling the conjugation length in the polymer.

Polythiophene device embodiment:
A film of the non-cross linked polythiophene was spun (1000 rpm/40sec) on a ITO coated glass substrate producing a dark red uniform film. The substrate is baked at 200°C for 60 minutes in vacuum (5 10^{-6} mbar). After cooling the film was carefully washed with chloroform and dried in nitrogen. 1000 A of aluminium is evaporated onto the polymer to form the top contact. Finally the device was encapsulated with an epoxy/glass combination. Figure 16 shows a typical IV and LI curve. 2 cd/sqm emission was observed at about 100mA/sqcm with 10V drive. The emission is red and the emission spectrum is shown in Figure 17.

In a further embodiment of this invention the UV/VIS properties of the crosslinked polymers are retained and show response to the solvent environment without dissolving significantly. The solid films of the crosslinked polymers are all red, but are orange in contact with chloroform or other good solvents (toluene, THF), indicating solvation of the polymers. The absorption spectra for the 9:1 copolymer (45b) are shown (Figure 11). This property serves the function of allowing these polymer films to be used

in detection and sensing devices on account of their change in optical properties. Changes in chiroptical properties could also be detected in crosslinked polythiophenes carrying chirally modified side chains. In this way, optical devices can be made which would function as sensors or chiral thin film affinity surfaces for detection of various substrates, such as enantiomers, peptides, proteins and enzymes.

Crosslinked cinnamate ester derivates

Poly(methacrylate) polymers **49** (Scheme 12) carrying statistical oxadiazole side chains, with distyrylbenzene and cinnamate side chains have been cross linked by photochemical irradiation. The resulting polymer in a light emitting device emits light blue light efficiently.

Poly(methacrylates) have many advantages such as high transparency, high resistance to chemicals, and good mechanical strength. It is also relatively easy to synthesise high molecular weight polymers as well as multi-functional copolymers. A range of aromatic oxadiazole bonded polymers, distyrylbenzene bonded polymers, and the copolymers bonded with both oxadiazole and distyrylbenzene have been synthesised and used for electron transporting layer or light emitting layer. However, the device of these polymers tend not to be very stable while working, presumably due to the flexible backbone and easy dimerisation between different distyrylbenzene. In order to overcome this problem, another functional unit that is UV-photosensitivity crosslinkable, has been copolymerised to achieve polymethacrylate with electron transporting unit, blue light emitting unit and UV-crosslinkable unit. Better device stability will be expected as the result of cross linking and therefore suppress polymer chain movement and dimerisation.

The UV-sensitive 2-(cinnamoyloxy) ethyl methacrylate **47** was synthesised according to the literature[M.Kato, T.Hirayama, *Macromol.Rapid.Commun.*, 1994, *15*, 741]. Monomer **47** can be readily polymerised in the initiating of AIBN. It was found when benzene is used as solvent, large majority of the formed

polymer is insoluble in common organic solvent, indicating the cross link reaction has been simultaneously resulted during polymerisation. When the polymerisation is carried out in THF, fully soluble polymer can be obtained at 60 °C for 8 hours. The solvent THF obviously not only plays a solubilising role, but also controls the reactivity of radical species.

The copolymerisation of the aromatic oxadiazole unit **46**, distyrylbenzene unit **48** and the monomer **47** was carried out under a similar conditions for the homopolymer. The ratio among the monomers can be varied. For convenience, equal weights of the monomers have been used for the copolymerisation that corresponds to p = 0.53, q = 0.28 and r = 0.19 (Scheme 12). Yellow powdery copolymer **49** can be obtained in good yield after purification (precipitate twice in methanol). The copolymer **49** is soluble in chlorinated solvents, THF and toluene but insoluble in hexane, methanol. GPC analysis revealed that the molar mass of **49** is 11,200/53,500(M_n/M_w). Free standing polymer film can be easily obtained by casting technique. The polymer has good stability if it is kept in the refrigerator at < 0 °C.

The polymer **49** fluoresces greenish blue under UV light.

The photocrosslinking behaviour of the copolymer 49

The three unit copolymer contains not only a luminophore and an electron transporting chromophore, but also a UV-sensitive cross linking unit. In order to understand the photocrosslinking behaviour of the polymer, a thin film of the polymer was exposed in UV-light for various time. It can be seen from Figure 14 that the copolymer exhibits 3 absorption peaks in the solid state at 200 nm, 295 nm and 400 nm. With increasing exposure time, the intensity of these 3 peaks decreased. The peaks at 295 nm and 200 nm are related to the cinnamoyloxy group which will be decreased as the result of cross linking. The effect on the IR absorption of the

cinnamoyl ester carboxyl group is seen in Table 2. When a film polymer **49** (on a glass plate) was exposed for 5 minutes, the film became insoluble in chloroform but still fluoresced blue. Therefore, 5-10 minutes exposure time was appropriate for obtaining a cross linked and insoluble polymer. The PL spectrum of the resulting cross-linked polymer film showed little change upon further irradiation and maintained constant luminescence efficiency (39%).

Time /m	0	1	6	16	26	40	60	80	110
IR peak (cm-1)	1722	1722	1723	1724	1725	1727	1728	1729	1729

Table 2: The change of ester group infrared absorption with UV exposure time

LED application

Two LED devices have been fabricated using PPV as hole transporting layer and copolymer **49** with and without UV irradiation (5 minutes) as emissive layer:

A ITO/PPV/Polymer 49/Al: Pale blue emission (20 V/0.8 mA)

B) ITO/PPV/Polymer **49** irradiated/Al: Pale blue emission (28 V/0.8 mA)

The above results show that polymer **49** can be successfully used as a blue light emitting polymer using stable aluminium as cathode. Moreover, the spin-coated emissive polymer can be easily cured by UV irradiation to become insoluble which leads to crosslinked polymer and results in a more stable polymer LED.

A single layer light emitting device using the polymer **49** as an emissive layer and calcium as cathode has also been made. Blue light emission has been observed with 0.1% internal

quantum efficiency. For a single layer device, the quantum efficiency is relatively high. The electroluminescence spectrum of the single layer device using polymer **49** is shown in figure 15.

REPRESENTATIVE SYNTHESIS OF POLYMER 45b

<u>Regioregular 9:1 Poly{3-hexyl-co-3-(11-[2-tetrahydropyranyloxy]undecyl)-thi ophene} (**43b**)</u>

Following the above procedure (for polymer **43a**) a mixture of 2-bromo-3-hexylthiophene (**41**) (1.47 g, 5.95 mmol) and 2-bromo-3-(5-[2-tetrahydropyranyloxy]undecyl)-thiophene (**42**) (0.28 g, 0.67 mmol) was polymerised (with one addition of $NiCl_2$(dppp) catalyst) to give copolymer **43b** (108 mg, 9 %) as a deep purple solid film. λ_{max} ($CHCl_3$/nm) 450; δ_H (200 MHz, $CDCl_3$) 0.91 (t, J 6.4, 6′-H [3H] of hexyl), 1.20-1.80 (br m, side-chain CH_2), 2.81 (2H, br t, J 7.6, 1′-H), 3.31 - 3.54 (0.2H, m, 11′, 6′′-H [2H] of 11-THPO-undecyl), 3.66 - 3.90 (0.2H, m, 11′, 6′′-H [2H] of 11-THPO-undecyl) 4.57 (0.1H, m, 2"-H [1H] of 11-THPO-undecyl) and 6.98 (1H, s, 4-H); GPC ($CHCl_3$, 450 nm)/Da M_n 9,5000, M_w 13,400, polydispersity 1.42.

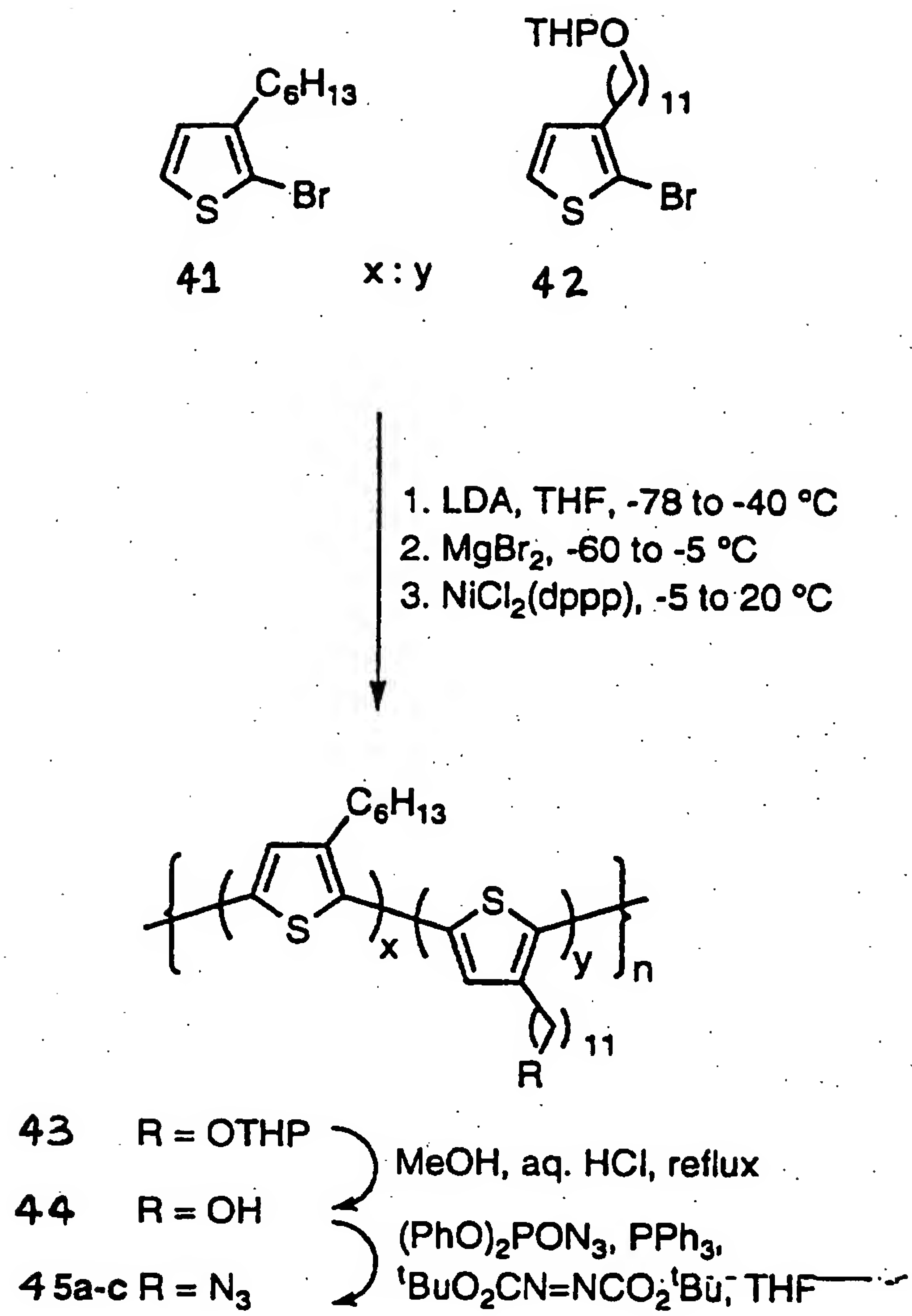
<u>Regioregular 9:1 Poly{3-hexyl-co-3-(11-hydroxyundecyl)thiophene} (**44b**)</u>

Following the above procedure (for polymer **44a**), regioregular 9:1 poly{3-hexyl-co-(11-[2-tetrahydropyranyloxy]undecyl)thiophene} (**43b**) (117 mg) was treated with methanol / dilute aqueous HCl to give deprotected copolymer **44b** (104 mg, 93 %) as a deep purple solid film. λ_{max} (solid/nm) 526, 550 sh, 600 sh, ($CHCl_3$/nm) 450; δ_H (200 MHz, $CDCl_3$) 0.91 (br t, J ~6.4, 6′-H [3H] of hexyl), 1.20-1.80 (br m, side-chain CH_2), 2.81 (2H, br t, J ~7.5, 1′-H), 3.62 (0.2H, t, J 6.5, 11′-H [2H] of 11-hydroxy-undecyl) and 6.98 (1H, s, 4-H); GPC ($CHCl_3$, 450 nm)/Da M_n 11,500, M_w 17,000, polydispersity 1.65.

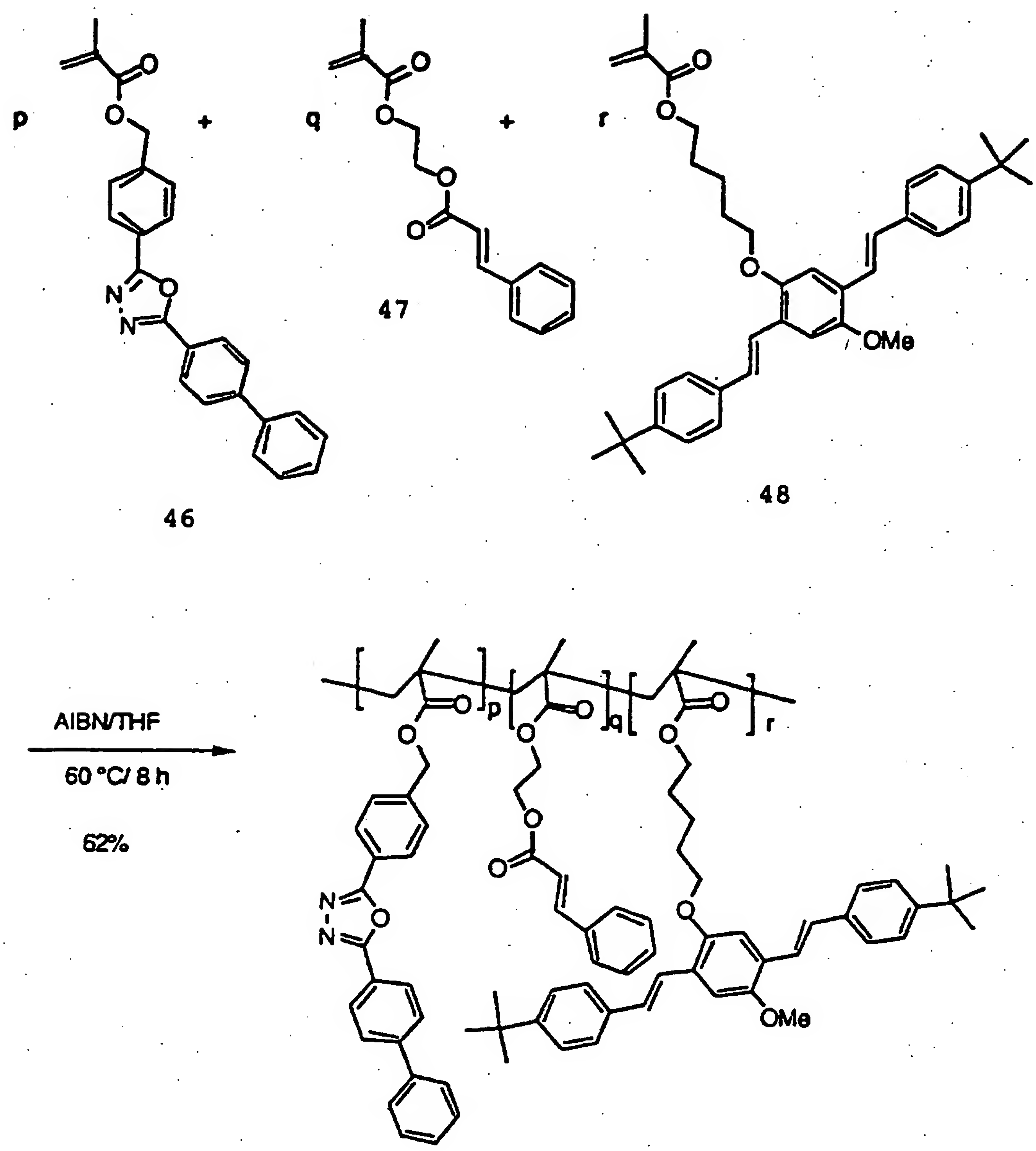
<u>Regioregular 9:1 Poly{3-hexyl-co-3-(11-azidoundecyl)thiophene} (**45b**)</u>

Following the above procedure (for polymer **45a**), regioregular

9:1 poly{3-hexyl-co-3-(11-hydroxyundecyl)thiophene} (**44b**) (77 mg) was azidated to give copolymer **45b** (63 mg, 81 %) as a deep purple solid film. λ_{max} (KBr disc)/cm^{-1} includes 2095 w (azide); λ_{max} (solid/nm) 522, 550 sh, 600 sh, ($CHCl_3$/nm) 450; δ_H (200 MHz, $CDCl_3$) 0.91 (br t, J ~6.7, 6'-H [3H] of hexyl), 1.20-1.80 (br m, side-chain CH_2), 2.81 (2H, br t, J ~7.4, 1'-H), 3.23 (0.2H, t, J ~7, 11'-H [2H] of 11-azidoundecyl) and 6.98 (1H, s, 4-H); GPC ($CHCl_3$, 450 nm)/Da M_n 5,100, M_v 11,800, polydispersity 2.34; DSC: exotherm at 185 °C, max. at 200 °C (not seen on second sweep - nitrene formation); TGA (%/°C) 99.5/185, 95.5/270, 55/480, <10/600 (N_2 loss = 1.6 %).


THPO
C_6H_{13}
Br
S
11
41
x : y
42
1. LDA, THF, -78 to -40 °C
2. $MgBr_2$, -60 to -5 °C
3. $NiCl_2$(dppp), -5 to 20 °C
x
y
n
R
43 R = OTHP
44 R = OH
45a-c R = N_3
MeOH, aq. HCl, reflux
$(PhO)_2PON_3$, PPh_3,
$^tBuO_2CN{=}NCO_2{}^tBu$, THF

Scheme 11



46 47 48

49

Scheme 12

CLAIMS:

1. A semiconductive polymer capable of luminescence in an optical device, which polymer comprises a luminescent film-forming solvent processible polymer which contains cross-linking so as to increase its molar mass and to resist solvent dissolution, the cross-linking being such that the polymer retains semiconductive and luminescent properties.

2. A polymer according to claim 1, wherein the cross-linking is formed by thermal cross-linking.

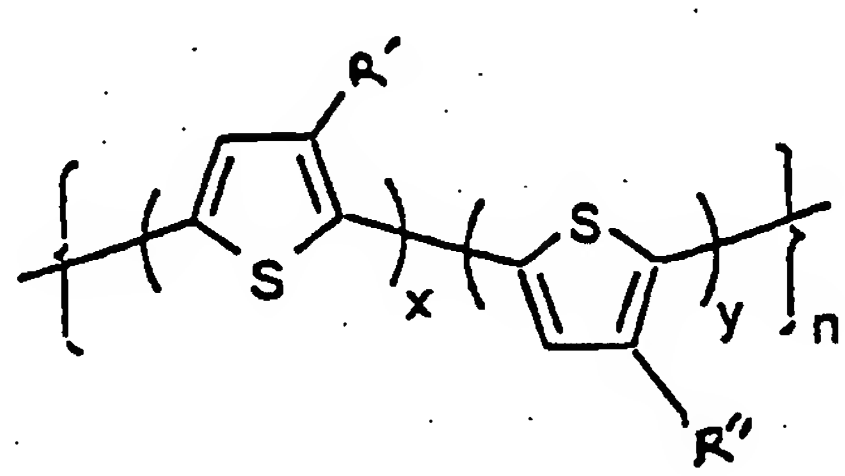
3. A polymer according to claim 1, wherein the cross-linking is formed by chemical cross-linking.

4. A polymer according to claim 1, wherein the cross-linking is formed by photochemical cross-linking.

5. A polymer according to any one of the preceding claims, which includes a luminescent main chain.

6. A polymer according to claim 5, wherein the main chain comprises a polythiophene copolymer capable of luminescence.

7. A polymer according to claim 6, wherein the polythiophene copolymer is of the general formula



in which R′ is a solubilising group, R″ is a spacer group cross-linking the main chain to another polymer, and x, y and n are each integers, wherein x:y is in the range 19:1 to 1:2 and n is in the range 3 to 100.

8. A polymer according to claim 7, in which R′ is $-C_6H_{13}$ and R″ comprises $-(CH_2)_{11}-$.

9. A polymer according to any one of claims 1 to 4, which includes a luminescent side chain.

10. A polymer according to claim 9, wherein the luminescent side chain is linked to the polymer main chain by a spacer.

11. A polymer according to claim 9 or claim 10, wherein the luminescent side chain comprises a distyryl benzene derivative.

12. A polymer according to any one of claims 9, 10 or 11, wherein the polymer comprises a polymethacrylate polymer capable of luminescence.

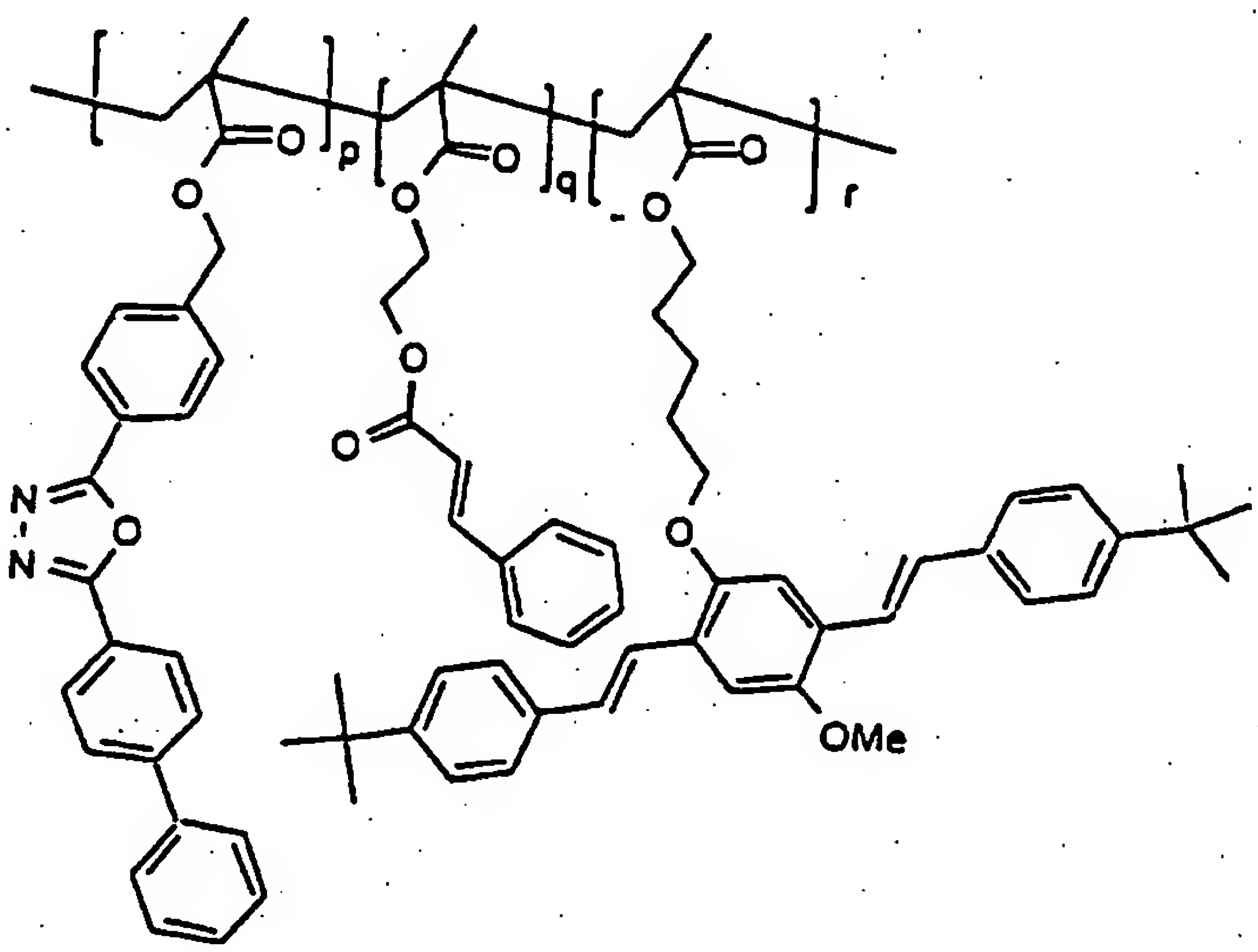
13. A polymer capable of charge transport in an optical device, which polymer comprises a film-forming polymer which is solvent processible or formed from a processible precursor polymer and which includes a charge transport segment in the polymer main chain or covalently linked thereto in a charge transport side chain.

14. A polymer according to any one of claims 1 to 12, which further comprises a charge transport segment as defined in claim 13.

15. A polymer according to claim 13 or claim 14, wherein the charge transport segment comprises the moiety Ar_1-Het-Ar_2 in which Ar_1 and Ar_2 are the same as or different from one

another and are each aromatic units; and Het is a heteroaromatic ring, the electronic structure of which favours charge transport.

16. A polymer according to claim 15, which comprises a luminescent polymer of general formula



which is cross-linked, in which p, q and r are independently each integers in the range 1 to 100.

17. Use of a polymer according to any one of the preceding claims in an optical device.

18. Use according to claim 17, wherein the optical device comprises an electroluminescent device.

19. An optical device which comprises a substrate and a polymer as defined in any one of the preceding claims supported on the substrate.

20. An optical device according to claim 19, which comprises an electroluminescent device.

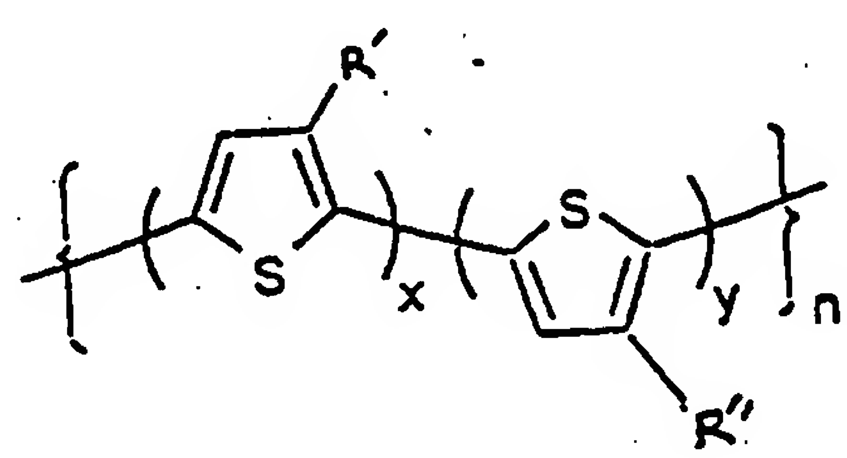
21. A process for the production of a semiconductive polymer, which process comprises providing a luminescent film-forming solvent processible polymer and cross-linking the solvent processible polymer under conditions so as to increase its molar mass whereby the polymer is made resistant to solvent dissolution and retains its semiconductive and luminescent properties.

22. A process according to claim 21, wherein the step of cross-linking the solvent processible polymer is effected by thermal cross-linking, chemical cross-linking or photochemical cross-linking.

23. A process according to claim 21 or claim 22, wherein the polymer includes a luminescent main chain.

24. A process according to claim 23, wherein the main chain comprises a polythiophene copolymer capable of luminescence.

25. A process according to claim 24, wherein the polythiophene copolymer is of the general formula



in which R′ is a solubilising group, R″ is a spacer group cross-linking the main chain to another polymer, and x, y and n are each integers, wherein x:y is in the range 19:1 to 1:2

1 and n is in the range 3 to 100.

26. A process according to claim 25, in which R′ is $-C_6H_{13}$ and R" comprises $-(CH_2)_{11}-$.

27. A process according to claim 21 or claim 22, wherein the polymer includes a luminescent side chain.

28. A process according to claim 27, wherein the luminescent side chain is linked to the polymer main chain by a spacer.

29. A process according to claim 28, wherein the luminescent side chain comprises a distyryl benzene derivative.

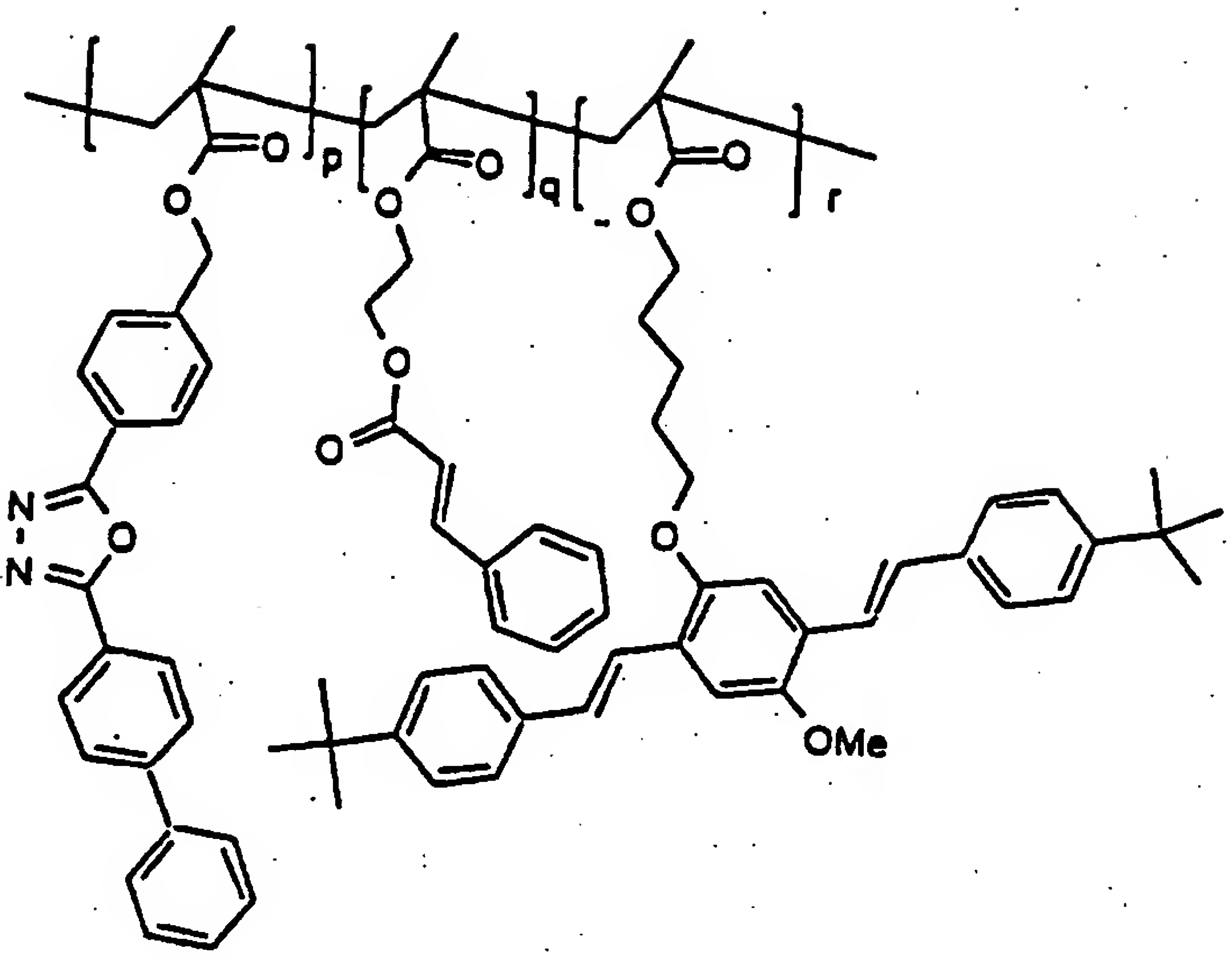
30. A process according to any one of claims 27 to 29, wherein the polymer comprises a polymethacrylate.

31. A process according to any one of claims 21 to 30, wherein the polymer includes a charge transport segment in the polymer main chain or covalently linked thereto in a charge transport side chain.

32. A process according to claim 31, wherein the charge transport segment comprises the moiety Ar_1-Het-Ar_2 in which Ar_1 and Ar_2 are the same as or different from one another and are each aromatic units; and Het is a heteroaromatic ring, the electronic structure of which favours charge transport.

33. A process according to claim 32, wherein the solvent processible polymer comprises a luminescent polymer of general formula

(58)



in which p, q and r are independently each integers in the range 1 to 100.

Fig. 1

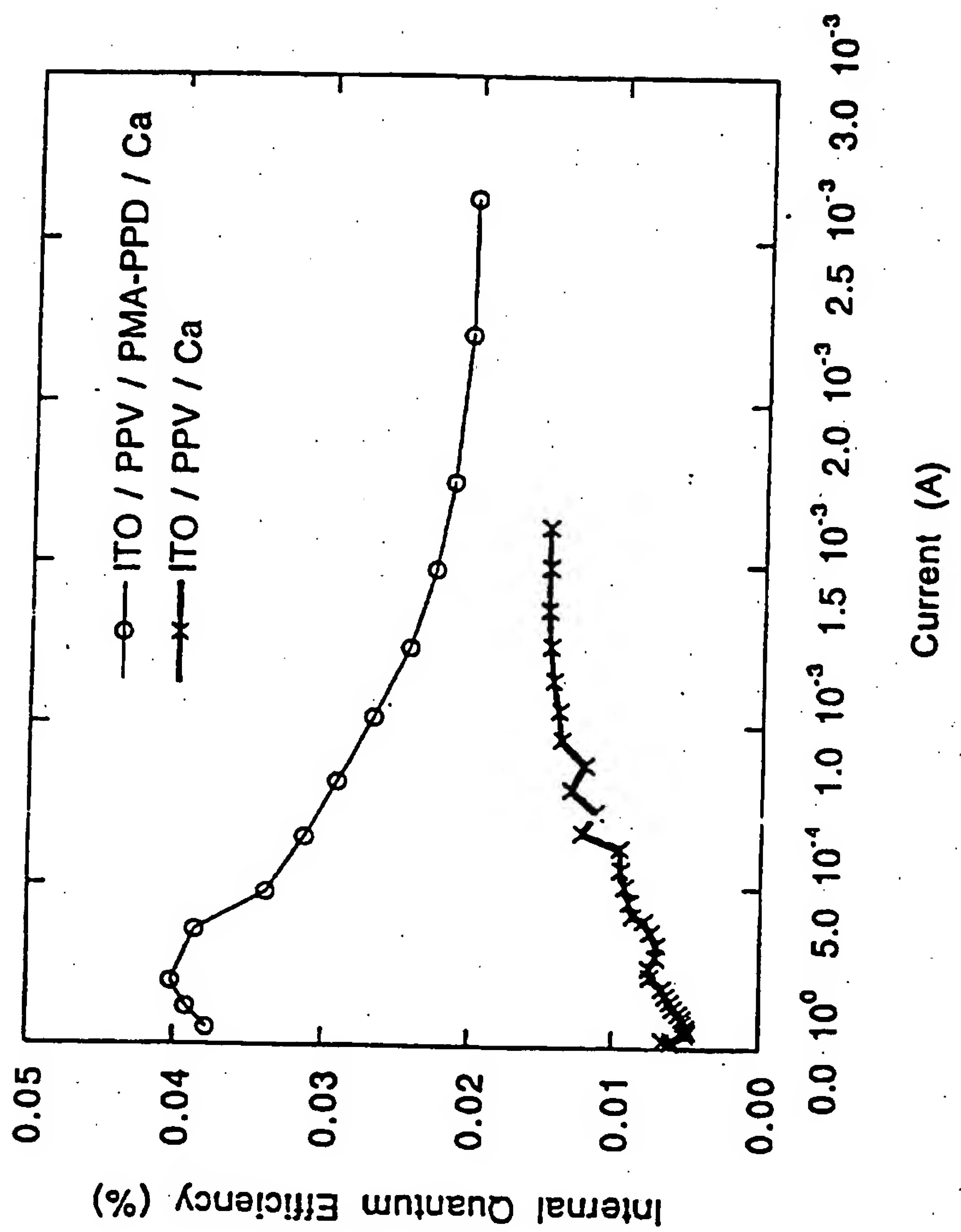

ITO / PPV / PMA-PPD / Ca
ITO / PPV / Ca
Internal Quantum Efficiency (%)
0.05
0.04
0.03
0.02
0.01
0.00
Current (A)
0.0 10^0
5.0 10^-4
1.0 10^-3
1.5 10^-3
2.0 10^-3
2.5 10^-3
3.0 10^-3

Fig. 2

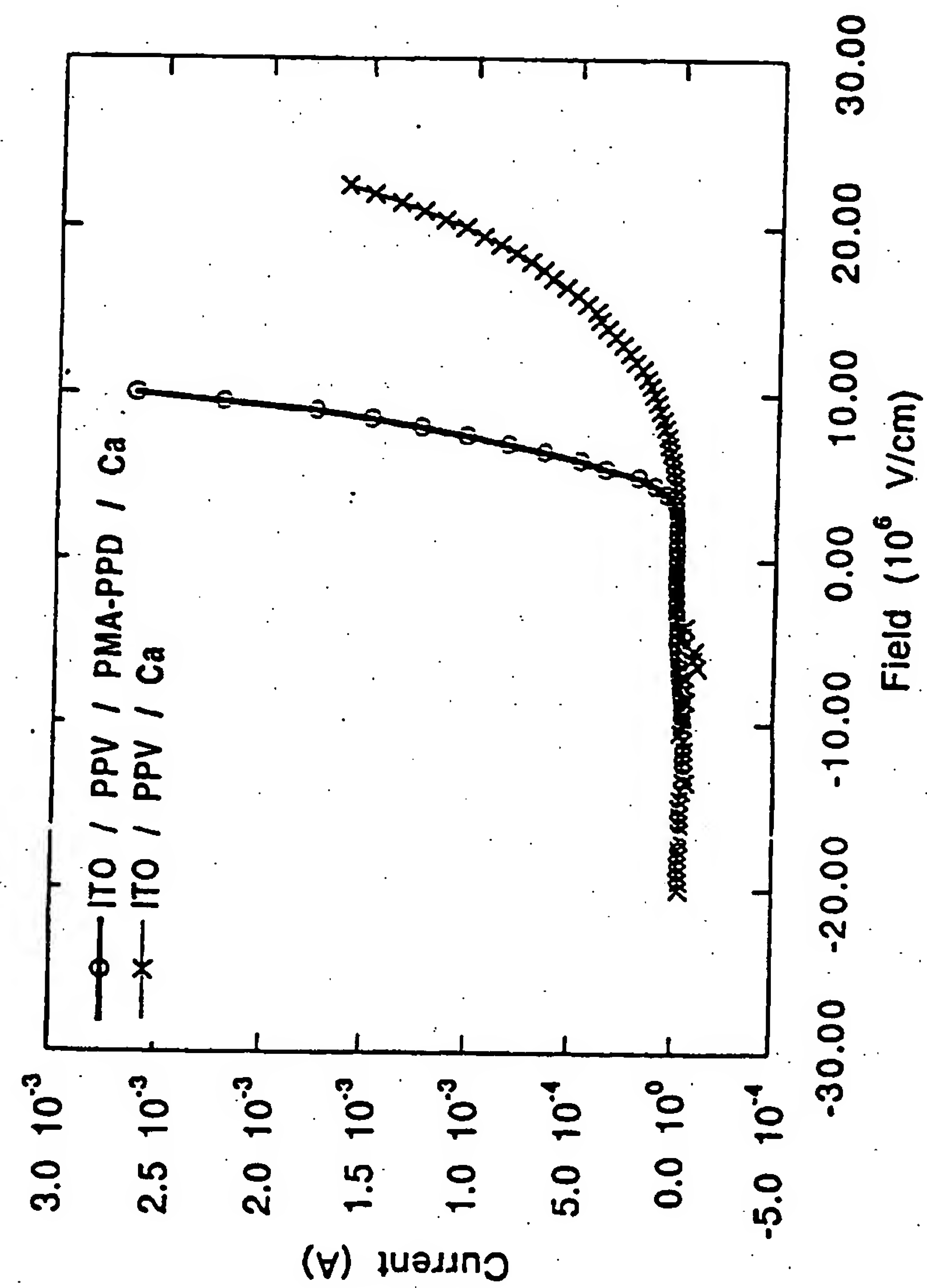

ITO / PPV / PMA-PPD / Ca
ITO / PPV / Ca
Current (A)
3.0 10^-3
2.5 10^-3
2.0 10^-3
1.5 10^-3
1.0 10^-3
5.0 10^-4
0.0 10^0
-5.0 10^-4
Field (10^6 V/cm)
-30.00
-20.00
-10.00
0.00
10.00
20.00
30.00

Fig. 3

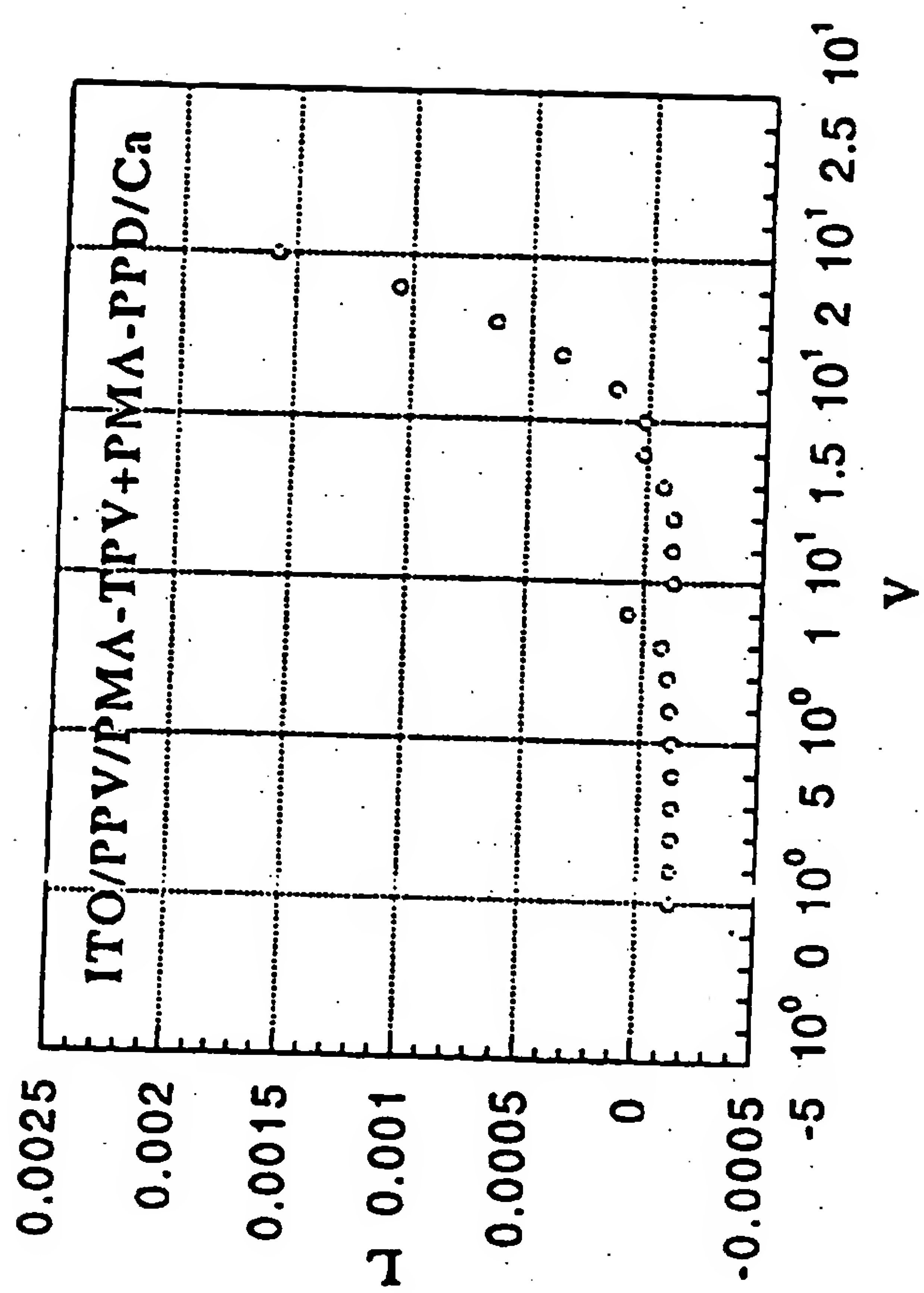

ITO/PPV/PMA-TPV+PMA-PPD/Ca
I
V
0.0025
0.002
0.0015
0.001
0.0005
0
-0.0005
-5 10⁰
0 10⁰
5 10⁰
1 10¹
1.5 10¹
2 10¹
2.5 10¹

Fig. 4

ITO/PPV/PMA-TPV+PMA-PPD/Ca

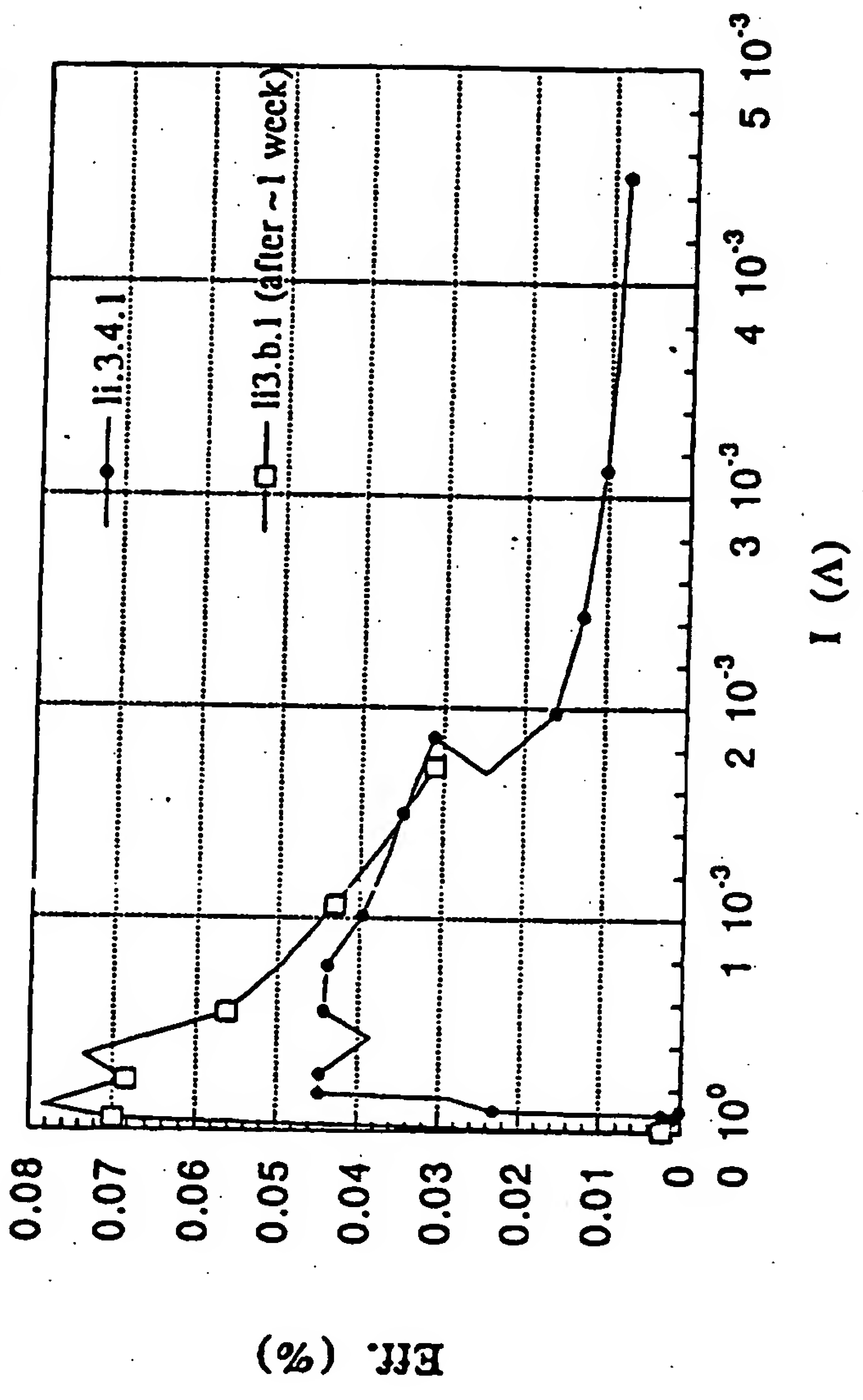


Fig. 5 ITO/PPV/PMA-TPV+PMA-PBD/Ca

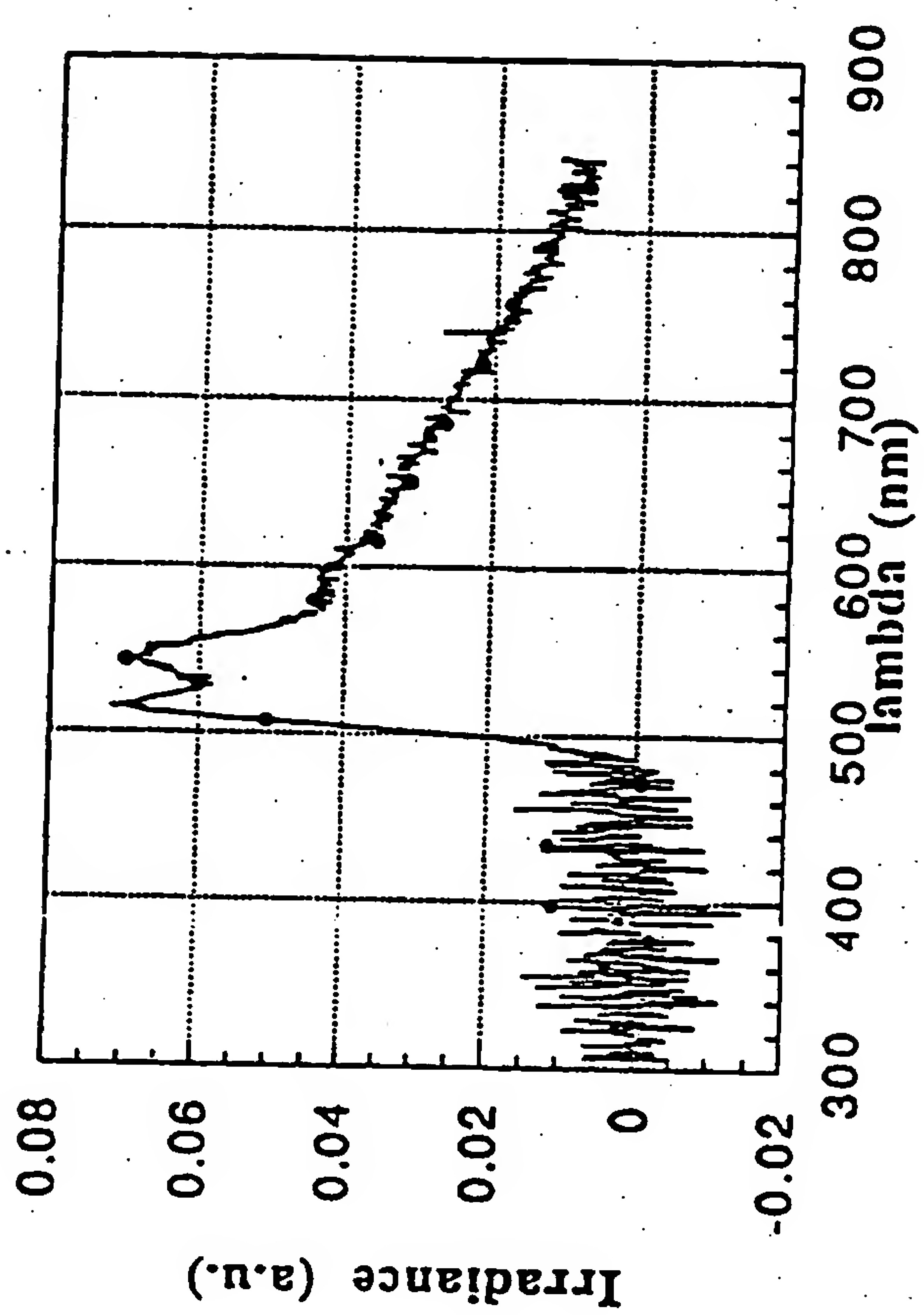


Fig. 6 ITO/PPV/PMA-TPV-PBD/Al

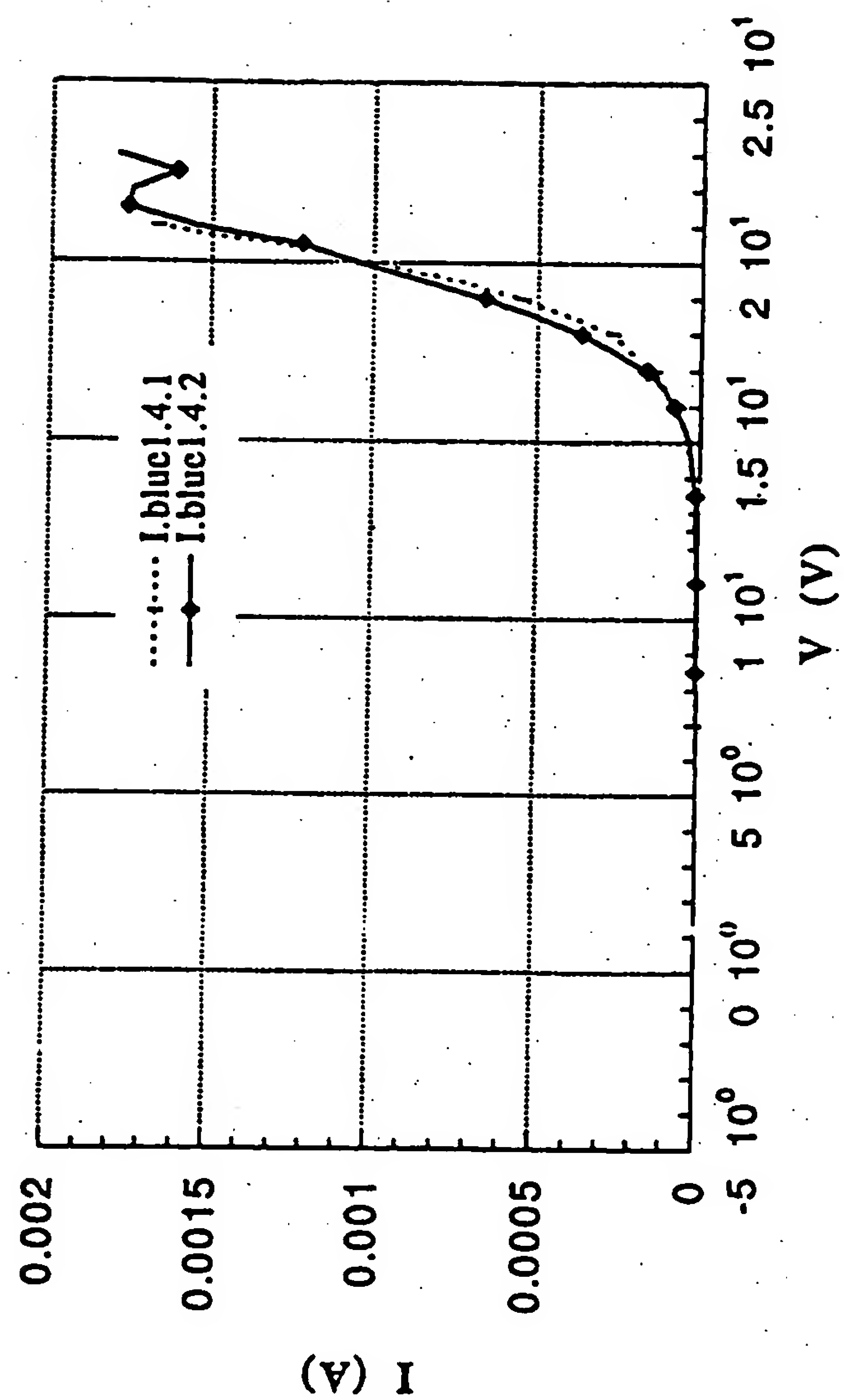


Fig. 7

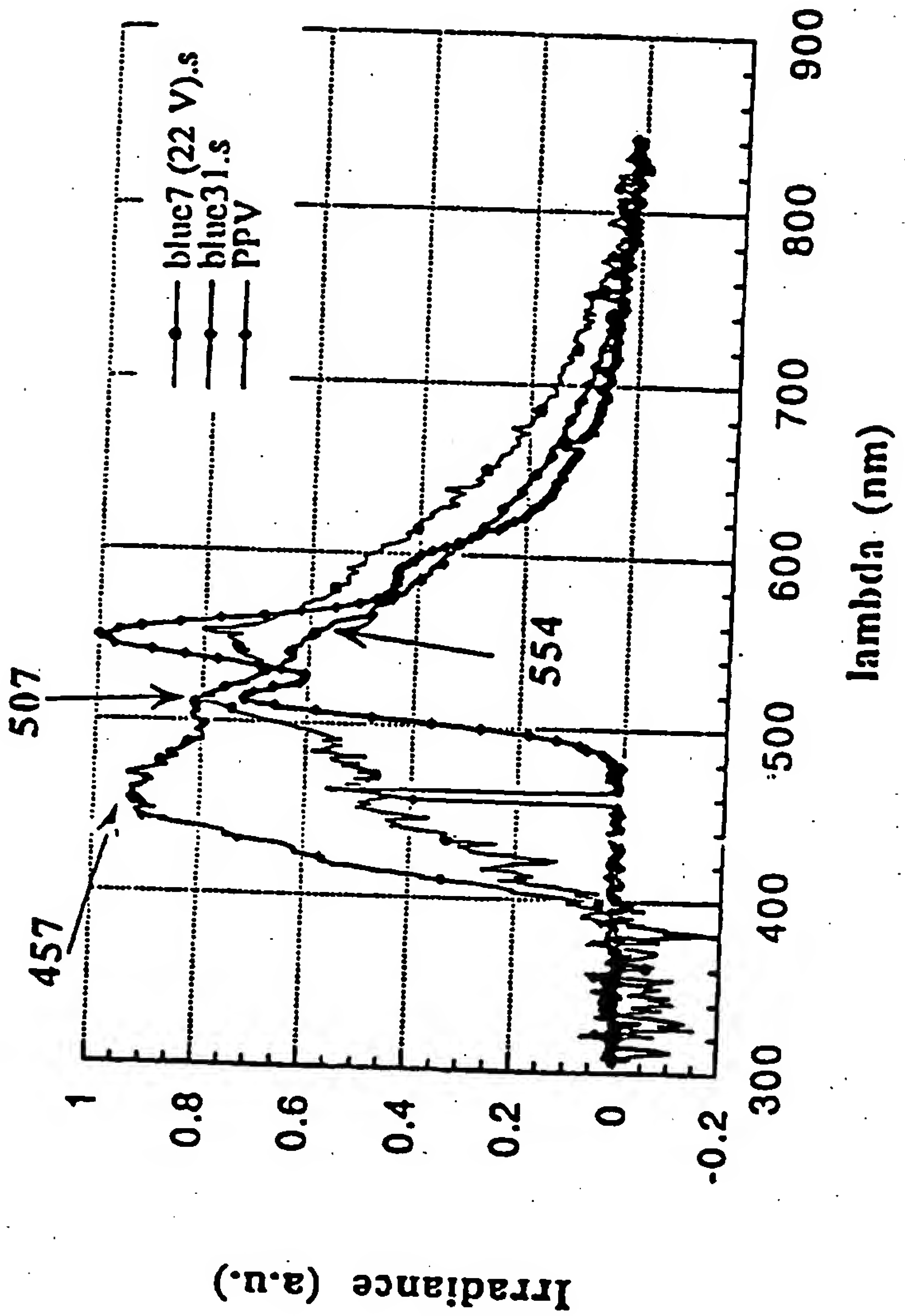

blue7 (22 V).s
blue31.s
PPV
457
507
554
Irradiance (a.u.)
1
0.8
0.6
0.4
0.2
0
-0.2
300
400
500
600
700
800
900
lambda (nm)

Fig. 8 ITO/PPV/Copolymer/Al

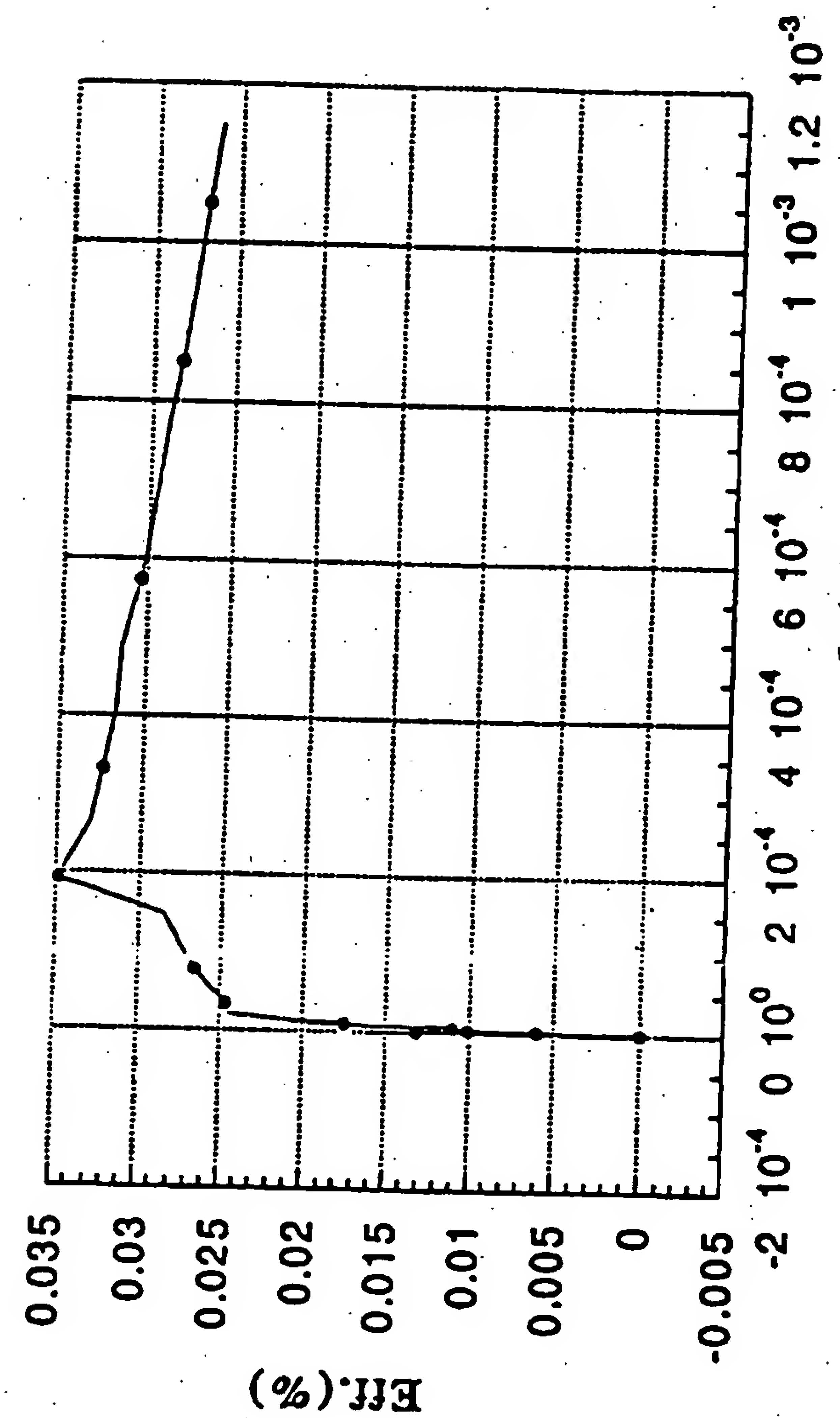
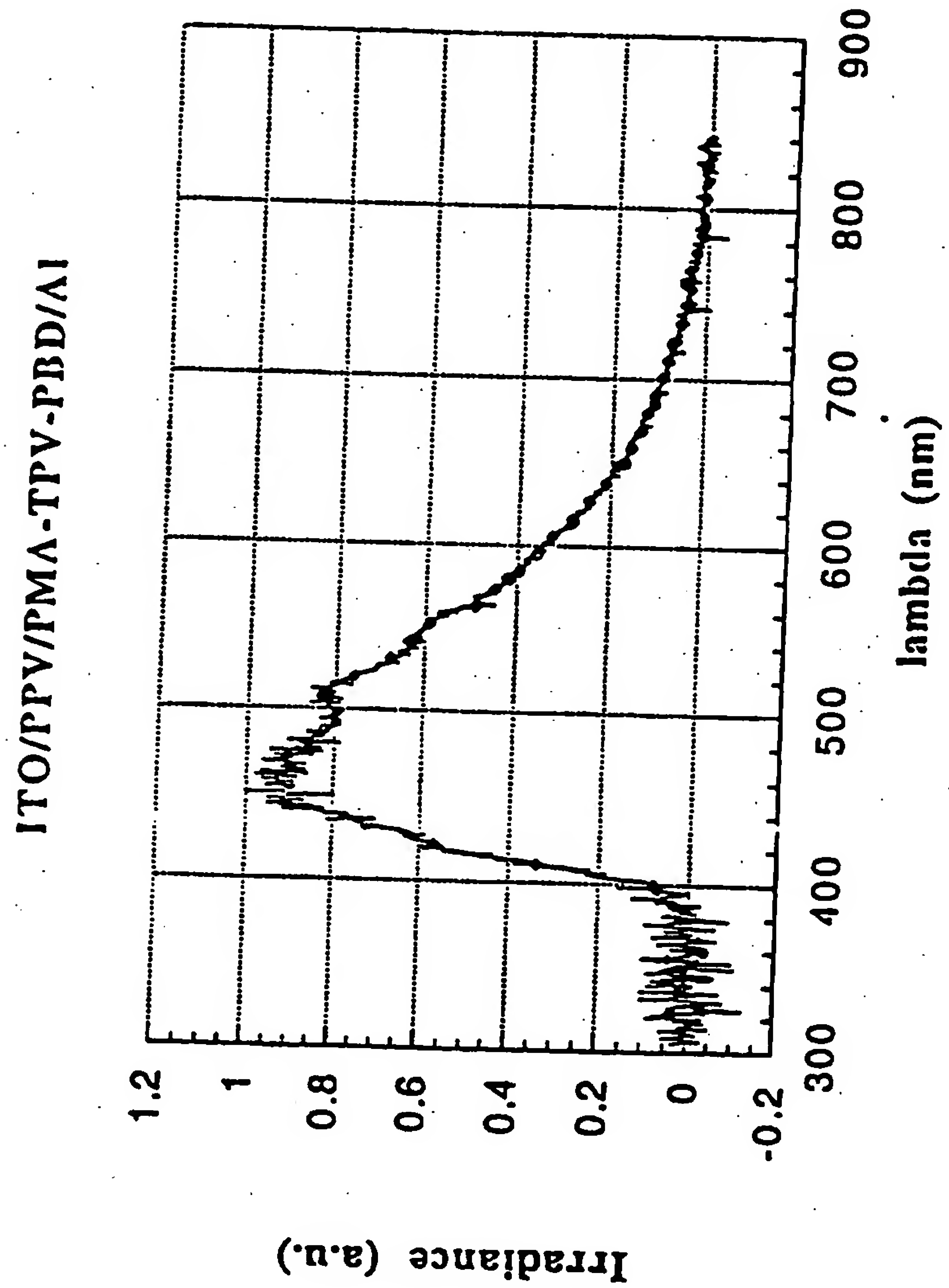


Figure 9


ITO/PPV/PMA-TPV-PBD/Al
lambda (nm)
Irradiance (a.u.)
300
400
500
600
700
800
900
-0.2
0
0.2
0.4
0.6
0.8
1
1.2

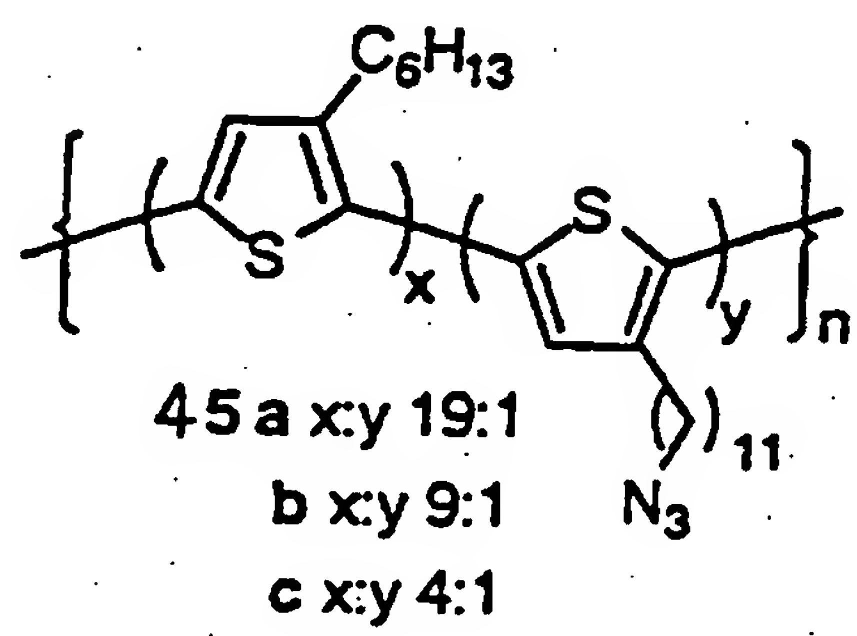


Figure 10 Representative polythiophenes for cross linking

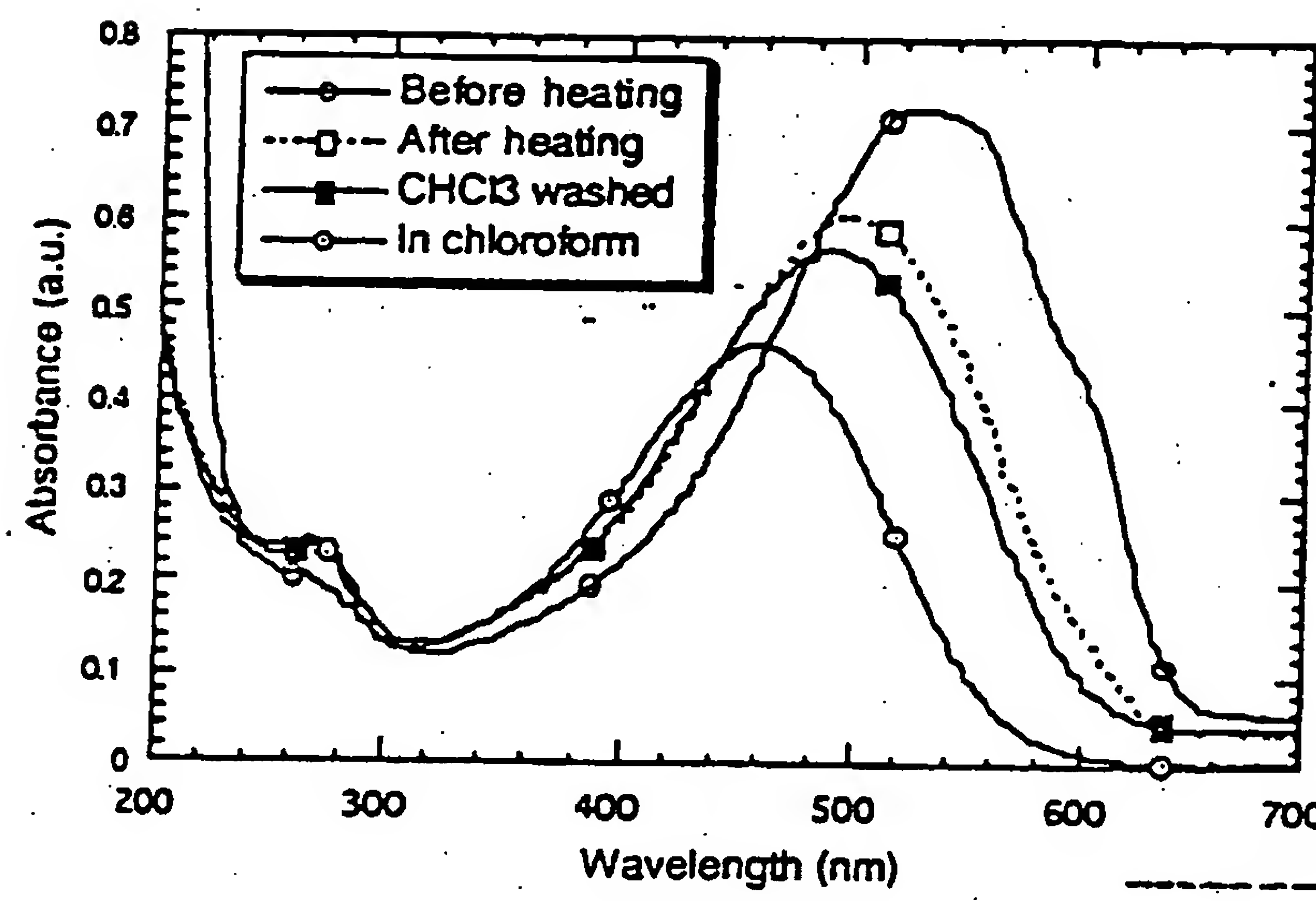


Figure 11: cross linking of 9:1 copolymer 45b; before heating (open circles), after 30 mins. at 200 °C, 0.1 mmHg (open squares, dotted), after washing with chloroform (solid squares) and the same, in contact with chloroform (dot circles).

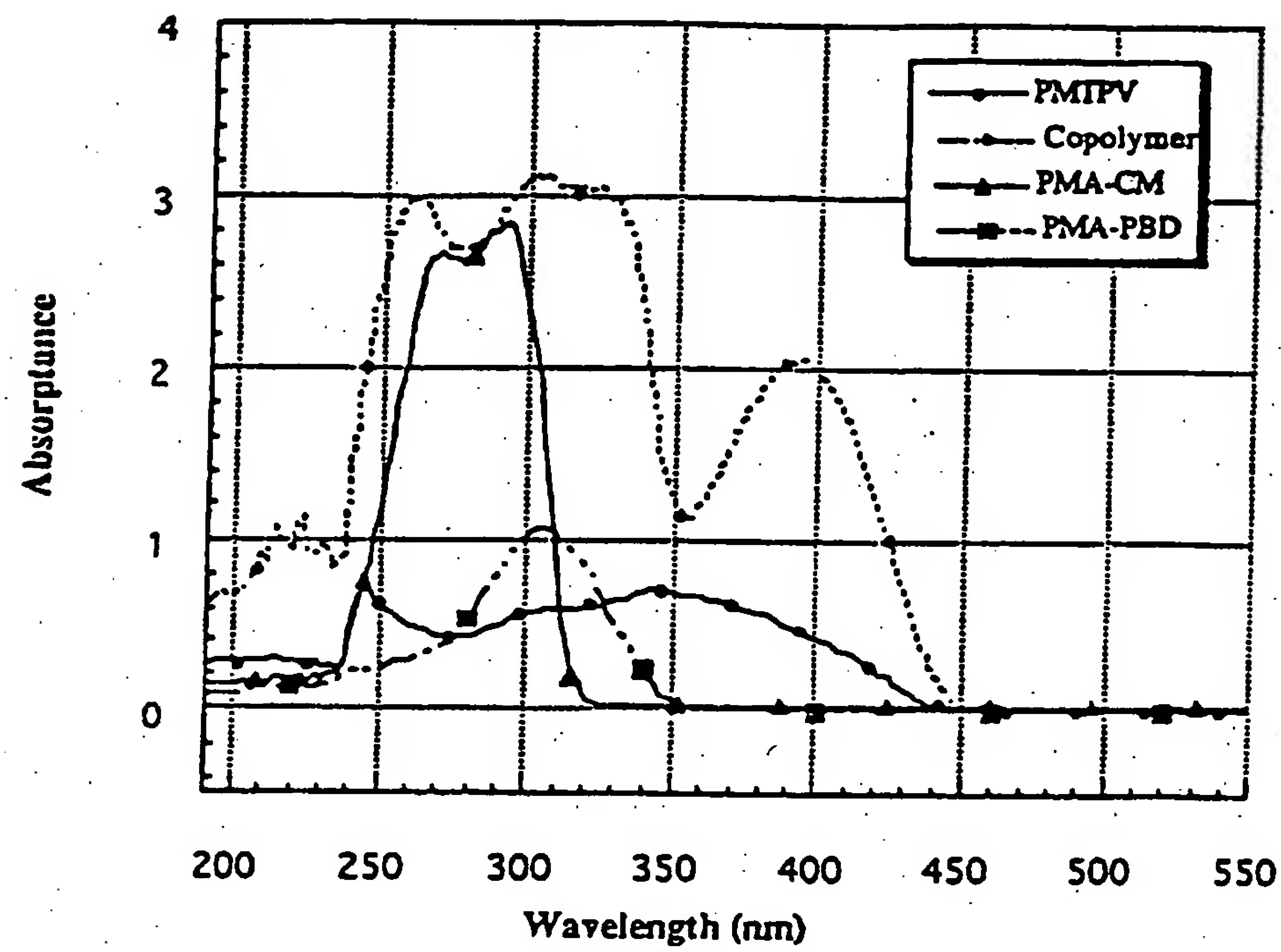


Figure 12:UV-VIS absorption spectra of *inter al.* copolymer 49 (-------).

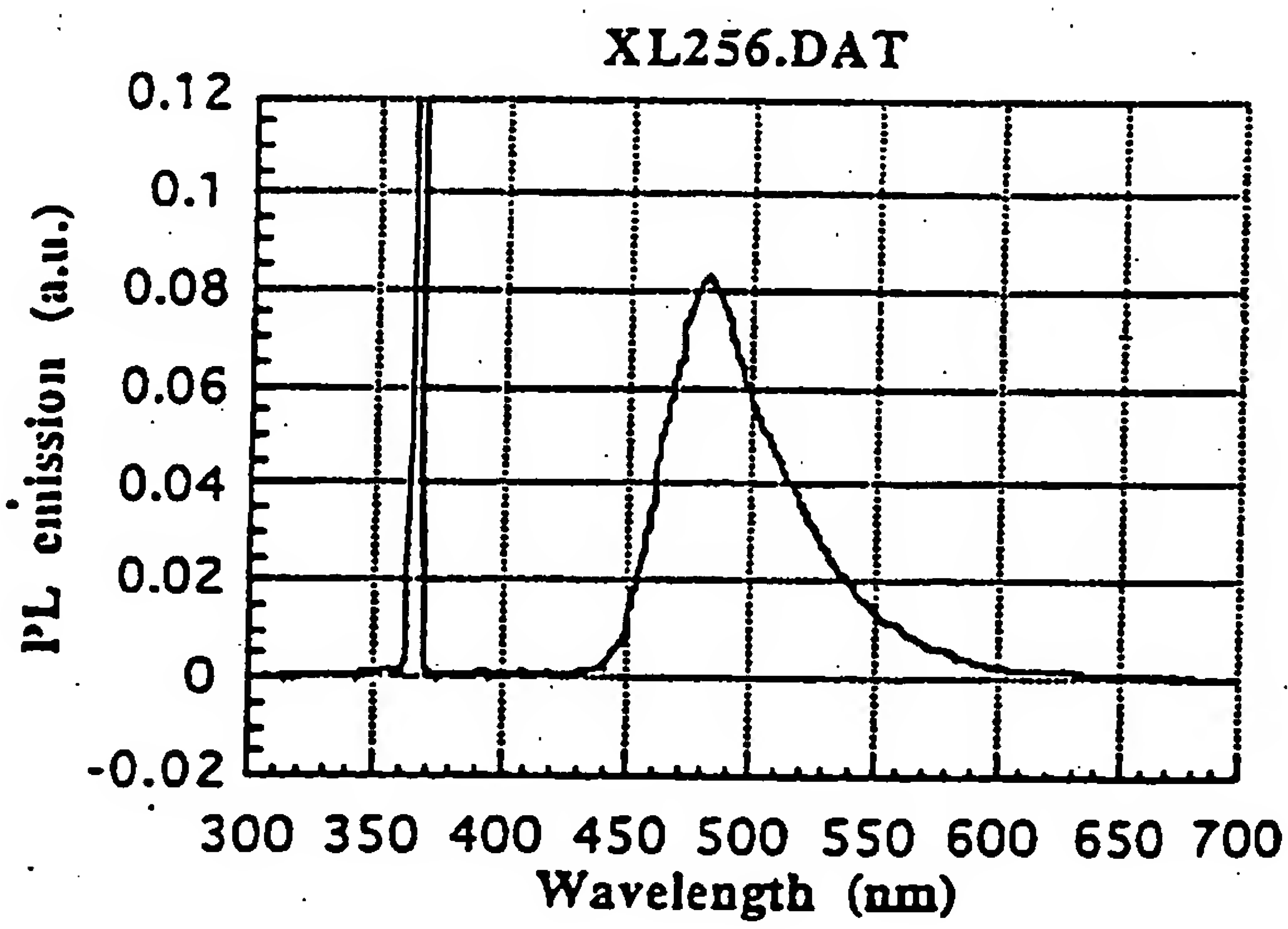


Figure 13: Photoluminescence spectrum of polymethacrylate 49 with 3 functional groups.

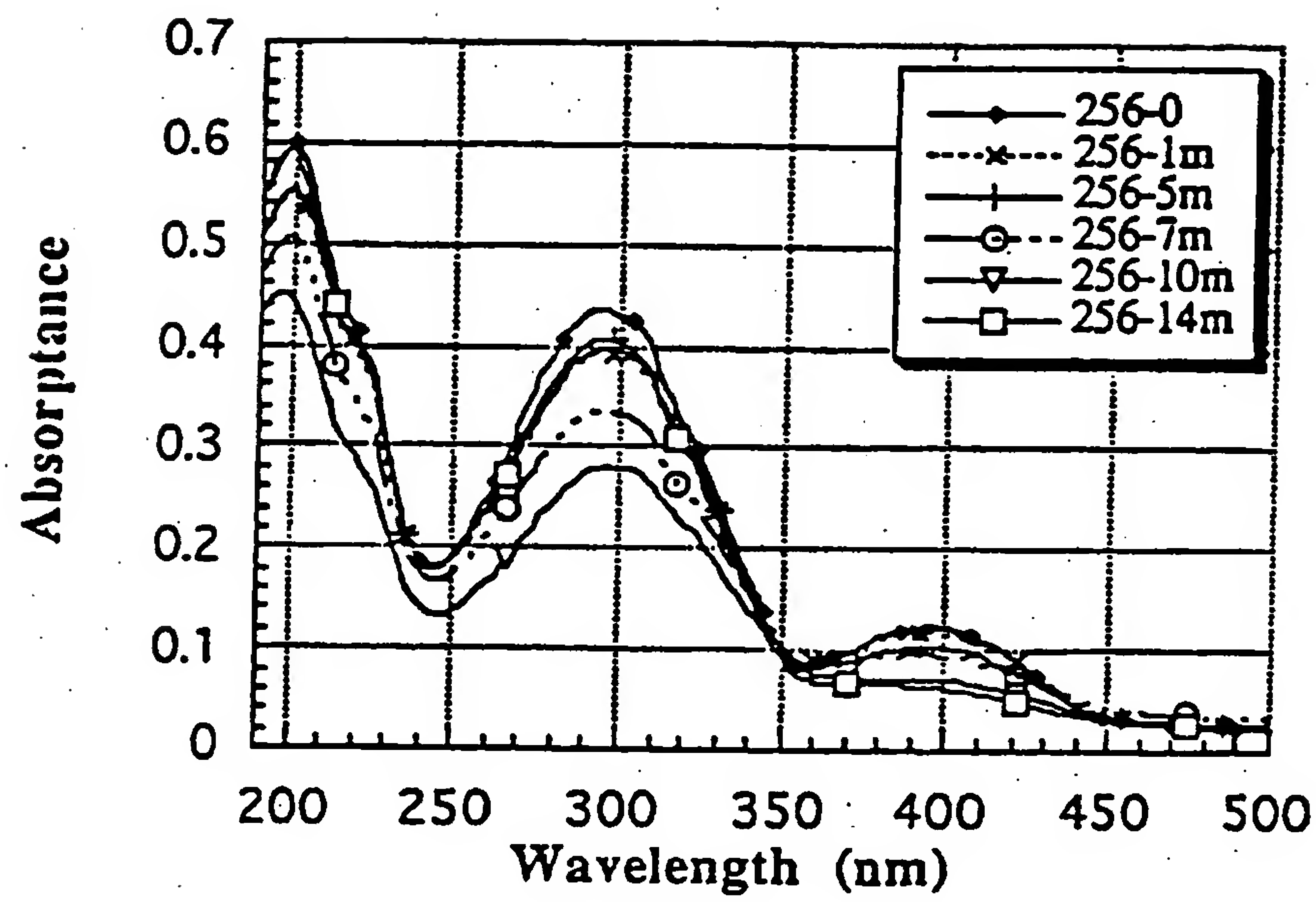


Figure 14 UV-VIS absorption change vs. UV light exposure time of the 3-unit copolymer

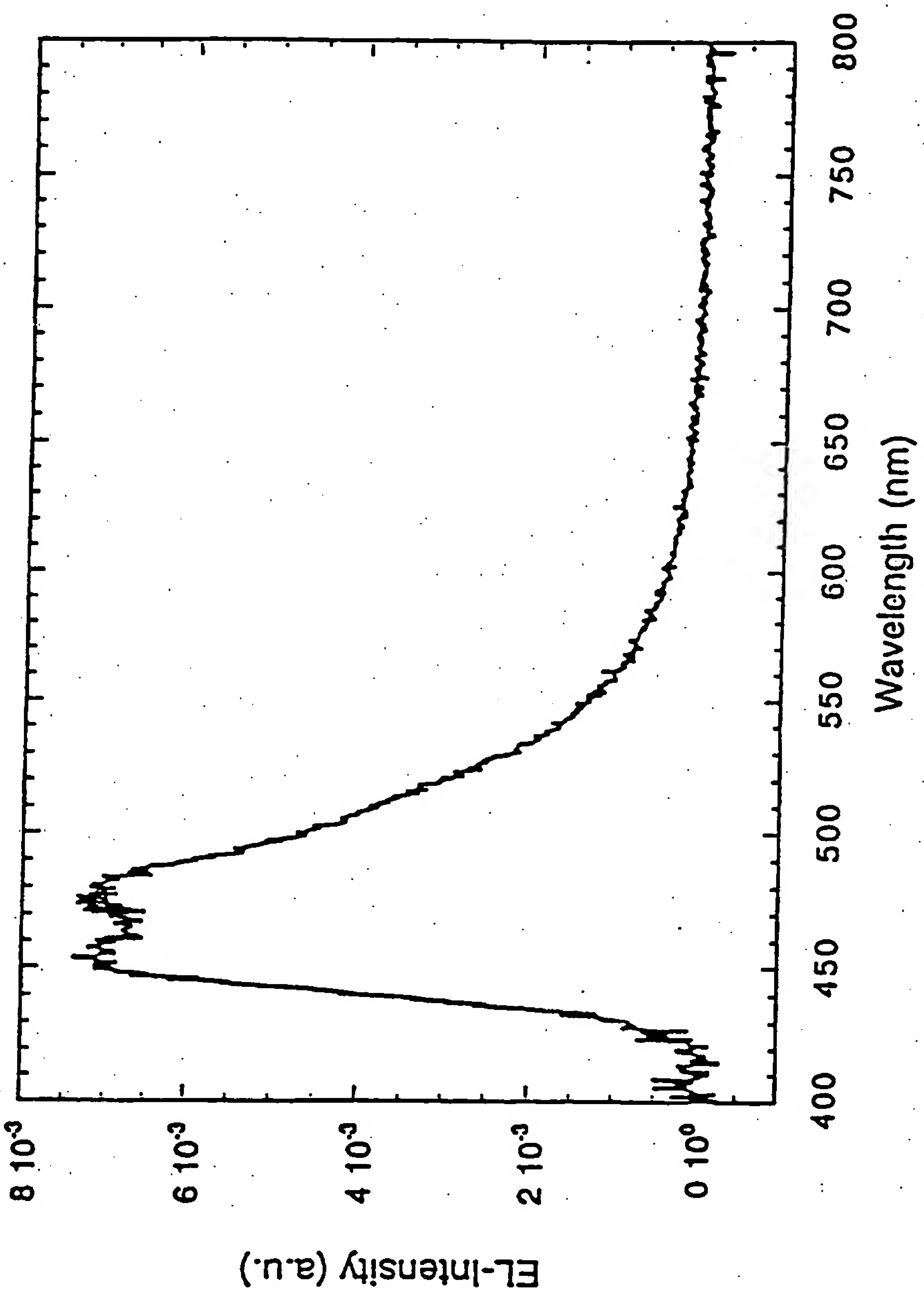


Figure 15: The Electroluminescence Spectrum of the LED using polymer 49 as an emissive layer.(ITO/Polymer 49/Ca, with internal quantum efficiency of 0.1%)

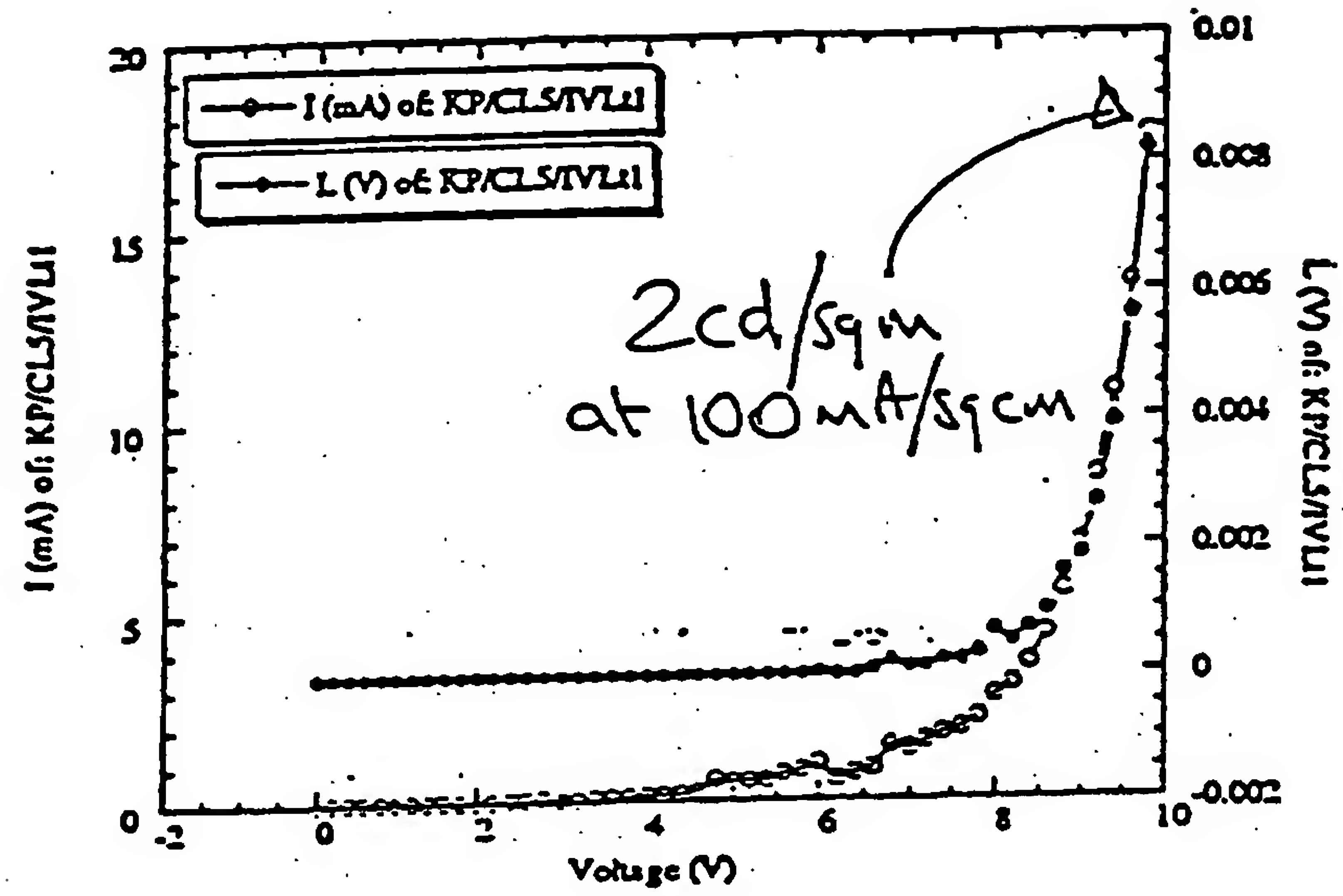


FIGURE 16

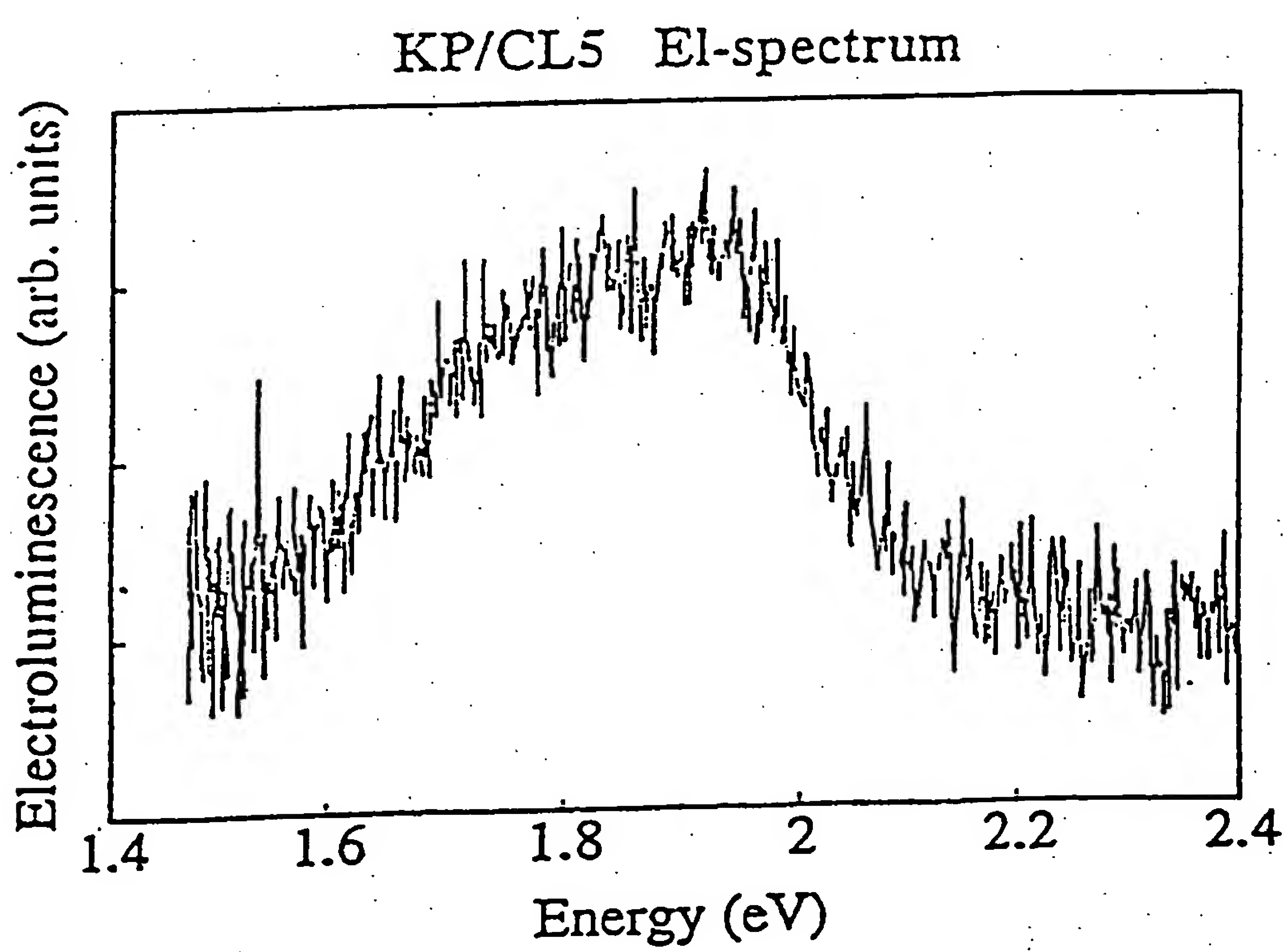


FIGURE 17

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 95/03043

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09K11/06 H05B33/14 H01L33/00 H05B33/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09K H05B H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,94 29883 (CAMBRIDGE DISPLAY) 22 December 1994 see the whole document ---	1,5,13, 14,17-20
A	WO,A,94 15441 (CAMBRIDGE DISPLAY TECHNOLOGY) 7 July 1994 see the whole document ---	1,3,5, 12,17-20
A	WO,A,93 14177 (CAMBRIDGE DISPLAY TECHNOLOGY) 22 July 1993 see the whole document -----	1,5, 17-20

☐ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search	Date of mailing of the international search report
19 March 1996	- 2. 04. 96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Drouot, M-C

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 95/03043

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9429883	22-12-94	AU-B- 6729194	03-01-95
WO-A-9415441	07-07-94	AU-B- 5706994	19-07-94
WO-A-9314177	22-07-93	AU-B- 3361793	03-08-93

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(71) Applicant *(for all designated States except US)*: CAMBRIDGE DISPLAY TECHNOLOGY LIMITED [GB/GB]; 13 Station Road, Cambridge CB3 0DJ (GB).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: PICHLER, Karl [AT/GB]; 3 Victoria Park, Cambridge CB4 3EJ (GB).

(74) Agents: DRIVER, Virginia, Rozanne et al.; Page White & Farrer, 54 Doughty Street, London WC1N 2LS (GB).

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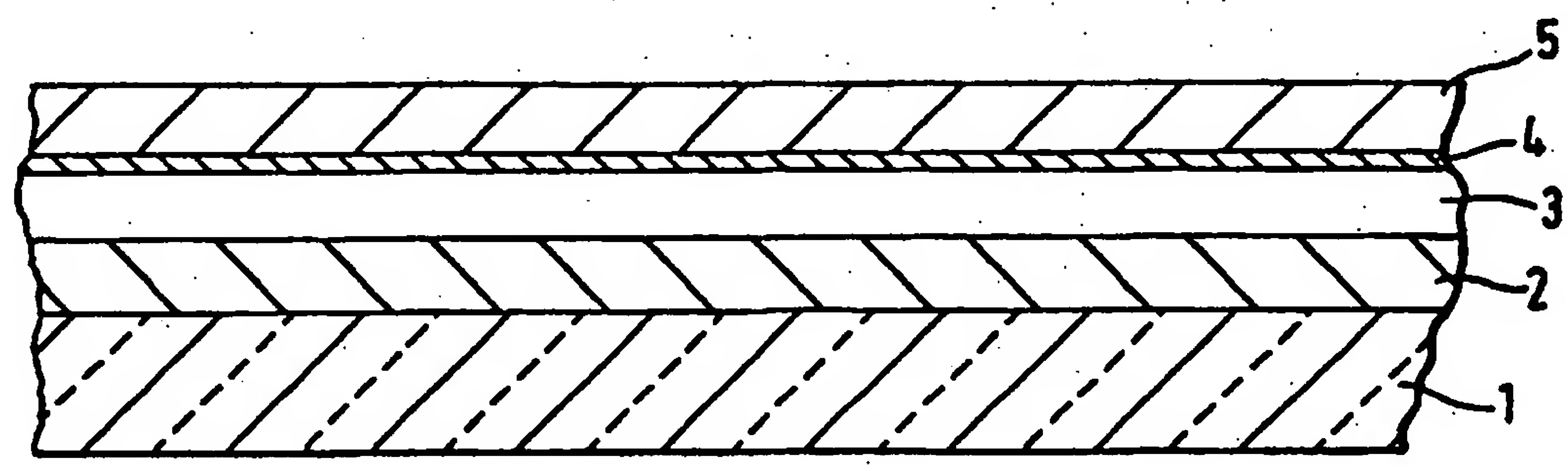

(57) Abstract

An organic light-emitting device wherein the cathode (4, 5) comprises a first layer (5) of a conducting material and a second layer (4) of a conductive material having a work function of at most 3,7 ev and wherein the second layer is substantially thinner than the first layer, having a thickness of at most 5 mm.

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ORGANIC LIGHT-EMITTING DEVICES WITH IMPROVED CATHODE

The field of the invention relates to organic light-emitting devices with efficient electron injecting electrodes.

Organic light-emitting devices (OLEDs) such as described in earlier US patent No. 5,247,190 assigned to Cambridge Display Technology Limited, or in Van Slyke et al., US No. 4,539,507, the contents of which are herein incorporated by reference and example, have great potential for use in various display applications. Principally, an OLED consists of an anode that injects positive charge carriers, a cathode that injects negative charge carriers and at least one organic electroluminescent layer sandwiched between the two electrodes. One of the key advantages of the OLED technology is that devices can be operated at low drive voltages, provided that suitable electro-luminescent organic layers, and electrodes with good efficiencies for the injection of positive and negative charge carriers, are used. Typically although not necessarily the anode is a thin film of, for example, indium-tin-oxide (ITO), which is a semi-transparent conductive oxide which is commercially readily available already deposited on glass or plastic substrates. The organic layer(s) is normally deposited onto the ITO-coated substrate by, for example, evaporation, or any one of spin-coating, blade-coating, dip-coating or meniscus-coating. The final step of depositing the cathode layer onto the top organic layer is normally performed by thermal evaporation or sputtering of a suitable cathode metal. Layers of Al, Ca or alloys of Mg:Ag or Mg:In or Al alloys are often used as cathode materials. In order to achieve good performance in OLEDs it is of great importance to optimise all individual layers, the anode, the cathode and the organic layer(s), as well as the interfaces between the layers.

It is very often found that the electron-injection properties of the cathode are particularly important to achieve efficient device operation. Due to the electronic structure of most organic electroluminescent materials it is very often necessary

to employ cathode materials with a low work function to achieve efficient electron injection and low operating voltages. Such cathodes for OLEDs are typically alkali metals such as Li, Na, K, Rb or Cs, alkaline earth metals such as Mg, Ca, Sr or Ba or lanthanides such as Sm, Eu, Tb or Yb. These materials tend to react very readily with oxygen and moisture and particular care has to be taken on handling and/or during and after deposition onto OLEDs. Often these low work function materials are deposited as cathode layers onto OLEDs in the form of alloys whereby other alloy constituents stabilise the cathode layer; typical such alloys are for example Mg:Al, Mg:In or Mg:Ag or Al:Li. When using some of these low work function elements, for instance Ca, K, Li or Sm in pure or alloy form as OLED cathode layers these elements can diffuse into the organic layer(s) and subsequently dope the organic layer(s), cause electrical shorts or quench photo-luminescence, and therefore generally deteriorate device performance.

It is thus an object of the present invention to provide a structure, and method of fabrication for, an organic light-emitting device that incorporates low work function elements as cathodes to achieve efficient injection of negative charge carriers and low operating voltage, but minimises at least some of the problems outlined above.

According to a first aspect of the present invention there is provided an organic light-emitting device, comprising at least one layer of a light-emissive organic material arranged between an anode and a cathode for the device, wherein the cathode comprises a first layer of a conductive material which is an opaque metallic layer of high conductivity and a second layer of a conductive material having a low work function arranged between the at least one layer of organic material and the first layer of conductive material, wherein the second layer of conductive material is substantially thinner than the first layer of conductive material, having a thickness of at most 5 nm, and comprises an elemental metal, an alloy or an intermetallic

compound having a work function of at most 3.7 eV.

Thus, the cathode is composed of a thin layer of an elemental metal, alloy or inter-metallic compound, with a work function of at most 3.7 eV, but preferably less than 3.2 eV. The cathode layer has a thickness of at most 5 nm, but preferably of between 0.5 and 2 nm thick. The thin, low work function cathode layer is preferably capped with another conductive layer, typically 100 - 500 nm thick, which provides high conductivity protection for the underlying thin, low work function layer, as well as environmental stability. Such a bi-layer electrode structure according to the first aspect of the present invention forms a cathode layer with efficient electron injection for an OLED with at least one electro-luminescent organic layer between said cathode layer and an anode layer, the anode layer for injecting positive charge carriers.

Such a structure prevents excessive doping and minimises the risk of shorting of the device structure and quenching of the electro-luminescence of the at least one layer of organic material.

The first aspect of the invention also provides a method of fabricating an organic light-emitting device, comprising the steps of forming a cathode for the device over a substrate, which step comprises forming a first layer of a conductive material of high conductivity over a substrate and forming a second layer of a conductive material having a low work function over the first layer of conductive material, wherein the first layer of conductive material is an opaque metallic layer and the second layer of conductive material is substantially thinner than the first layer of conductive material having a thickness of at most 5 nm, and comprises an elemental metal, an alloy or an intermetallic compound having a work function of at most 3.7 eV, forming at least one layer of a light-emissive organic material over the cathode and forming an anode for the device over the at least one layer of organic material.

The first aspect of the invention further provides a method of fabricating an organic light-emitting device, comprising the steps of forming an anode for the device over a substrate, forming at least one layer of a light-emissive material over the anode and forming a cathode for the device over the at least one layer of organic material, which step comprises forming a second layer of a conductive material having a low work function over the at least one layer of organic material and forming a first layer of a conductive material of high conductivity over the second layer of conductive material, wherein the first layer of conductive material is an opaque metallic layer and the second layer of conductive material is substantially thinner than the first layer of conductive material having a thickness of at most 5 nm, and comprises an elemental metal, an alloy or an intermetallic compound having a work function of at most 3.7 eV.

Thus there is also provided a method of fabrication for an OLED with an efficient electron-injecting electrode in which at least one electro-luminescent organic layer, preferably either polymeric or molecular, is deposited preferably onto a supportive substrate pre-coated with an anode. The organic layer is coated in one embodiment by vacuum evaporation, with a thin layer of conductive, low work function material. This layer is at most 5 nm but preferably between 0.5 and 2 nm thick, and still more preferably about 0.5 nm. This thin layer is typically, but not essentially, an alkali metal, alkaline earth metal or a lanthanide or an alloy or inter-metallic compound incorporating one or more of said alkali metal, alkaline earth metal or lanthanide elements. The thin low work function layer is then preferably covered with a thick conductive layer of typically 100 to 500 nm thickness which provides high conductivity, protection for the underlying thin low work function layer and environmental stability, and which is preferably applied by vacuum evaporation or sputter deposition.

According to a second aspect of the present invention there is provided an organic light-emitting device, comprising at least

one layer of a light-emissive organic material arranged between an anode and a cathode for the device, wherein the cathode comprises a first layer of a conductive material which is a DC magnetron sputtered metallic layer of high conductivity and a second layer of a conductive material having a low work function arranged between the at least one layer of organic material and the first layer of conductive material, wherein the second layer of conductive material is substantially thinner than the first layer of conductive material.

Such a structure provides advantages similar to those discussed above with reference to the first aspect of the present invention.

The invention will now be described with reference to a particular example as shown in the accompanying drawing, in which:

Figure 1 illustrates a structure of an OLED in accordance with the present invention.

According to the illustrated embodiment of the invention, an OLED is formed by first forming a semi-transparent anode deposited onto a transparent supportive substrate. The substrate is, for example, a thin sheet of glass or plastic such as polyester, polycarbonate, polyimide, poly-ether-imide or the like. Referring to Figure 1, a glass substrate 1 is covered with a layer of a semi-transparent conductive indium-tin-oxide (ITO) layer 2, typically about 150 nm thick with a sheet resistance of typically ≤ 30 Ohms/square. Although the semi-transparent anode shown in Figure 1 is a thin layer of conductive oxide such as indium-tin-oxide, it may alternatively be a doped tin-oxide or zinc-oxide.

The organic layer(s) deposited on top of the anode/substrate is/are preferably, but not necessarily, one or more layers of an electro-luminescent conjugated polymer such as described in

earlier US No. 5,247,190 assigned to Cambridge Display Technology Limited. Such organic layer is formed to a thickness typically of the order of 100 nm thick. Alternatively the organic layer(s) could be low molecular weight compounds such as described in US patent No. 4,539,507, or a combination of layer(s) of conjugated polymer(s) with layer(s) of low molecular weight compound(s). In Figure 1, the ITO layer is covered with a ca. 100 nm thick layer 3 of the electroluminescent polymer poly(*p*-phenylene vinylene), PPV, as for example described in US patent No. 5,247,190.

The cathode may be a thin layer of an alkali metal, alkaline earth metal or a lanthanide or an alloy or inter-metallic compound incorporating one or more of said alkali metal, alkaline earth metal or lanthanide elements. The cathode layer is at most 5 nm but preferably between 0.5 and 2 nm thick and examples for materials which may be used are Li, K, Sm, Ca or an Al:Li alloy. In the example of Figure 1, the PPV layer 3 is preferably covered with a 0.5 nm thick layer 4 of Li deposited by vacuum sublimation of the Li from a commercial Al:Li alloy.

The thin layer of the cathode may be sputter deposited, preferably by DC magnetron sputtering or RF sputtering. The thin layer of the cathode may also be evaporated, preferably by resistive evaporation or electron beam thermal evaporation.

The thin layer of the cathode, being a conductive material comprising either an elemental metal, an alloy or an intermetallic compound having a work function of at most 3.7 eV, and preferably at most 3.2 eV.

The thin layer is then preferably covered with a conductive layer of, for example, aluminium or an aluminium alloy which is typically between 100 and 500 nm thick, and preferably about 100 nm. In Figure 1, the thin layer 4 is, without breaking vacuum, preferably covered with a 150 nm thick layer 5 of Aluminium deposited by vacuum evaporation.

The thick conductive layer may be sputtered, preferably by DC magnetron sputtering or RF sputtering. The thick layer may also be evaporated by resistive evaporation or electron-beam thermal evaporation.
Preferably, the ratio of the thickness of the thick conductive layer to the thin layer is 20:1.

The layer thicknesses are controlled by a standard quartz crystal thickness monitor in combination with a shutter.

In an alternative arrangement, the two-layer cathode described with reference to Figure 1 is formed on the substrate, the at least one layer of a light-emissive organic material is formed over the cathode, and the anode formed over the at least one layer of light-emissive organic material.

The thin layer of Li provides excellent electron injection and low turn-on and operating voltage and, although diffusion of the Li from layer 4 into the PPV layer 3 with subsequent doping and quenching of electro-luminescence in the PPV is not prohibited, the limited thickness and hence amount of material of layer 4 prevents excessive doping and electro-luminescence quenching.

There thus has been described a device structure, and process of fabrication thereof, for an OLED with an efficient low work function electron-injecting cathode with minimised risk of excessive doping of the organic layer(s) by the low work function cathode, and therefore minimised risk of shorting of the device structure and quenching of electro-luminescence.

Claims:

1. An organic light-emitting device, comprising at least one layer of a light-emissive organic material arranged between an anode and a cathode for the device, wherein the cathode comprises a first layer of a conductive material which is an opaque metallic layer of high conductivity and a second layer of a conductive material having a low work function arranged between the at least one layer of organic material and the first layer of conductive material, wherein the second layer of conductive material is substantially thinner than the first layer of conductive material, having a thickness of at most 5 nm, and comprises an elemental metal, an alloy or an intermetallic compound having a work function of at most 3.7 eV.

2. An organic light-emitting device according to claim 1, wherein the second layer of conductive material has a thickness in the range of from 0.5 to 2 nm.

3. An organic light-emitting device according to claim 1 or claim 2, wherein the second layer of conductive material has a thickness of about 0.5 nm.

4. An organic light-emitting device according to any one of claims 1 to 3, wherein the first layer of conductive material has a thickness in the range of from 100 to 500 nm.

5. An organic light-emitting device according to claim 4, wherein the first layer of conductive material has a thickness of about 150 nm.

6. An organic light-emitting device according to any of claims 1 to 5, wherein the first layer of conductive material comprises Al or an alloy thereof.

7. An organic light-emitting device according to any of claims 1 to 7, wherein the second layer of conductive material comprises

an elemental metal, an alloy or an intermetallic compound having a work function of at most 3.2 eV.

8. An organic light-emitting device according to any of claims 1 to 7, wherein the second layer of conductive material comprises one of an alkali metal, an alkaline earth metal or a lanthanide, or an alloy or an intermetallic compound thereof.

9. An organic light-emitting device according to claim 8, wherein the second layer of conductive material comprises one of Ca, K, Li, Sm or an Al-Li alloy.

10. An organic light-emitting device according to any of claims 1 to 9, wherein the ratio of thicknesses of the first layer of conductive material to the second layer of conductive material is at least 20 : 1.

11. An organic light-emitting device according to any of claims 1 to 10, wherein the at least one layer of organic material has a thickness of about 100 nm.

12. An organic light-emitting device according to any of claims 1 to 11, wherein the organic material is a conjugated polymer.

13. An organic light-emitting device according to any of claims 1 to 11, wherein the organic material is a low molecular weight compound.

14. An organic light-emitting device according to any of claims 1 to 11, wherein the at least one layer of organic material comprises a composite structure including at least one layer of a conjugated polymer and at least one layer of a low molecular weight compound.

15. An organic light-emitting device according to any of claims 1 to 14, further comprising a substrate, wherein the anode is formed over the substrate and the cathode is formed over the at

least one layer of organic material.

16. An organic light-emitting device according to any of claims 1 to 14, further comprising a substrate, wherein the cathode is formed over the substrate and the anode is formed over the at least one layer of organic material.

17. An organic light-emitting device according to claim 15 or 16, wherein the substrate comprises one of a glass or a plastics material.

18. An organic light-emitting device according to claim 17, wherein the substrate comprises polyester, polycarbonate, polyimide or poly-ether-imide.

19. An organic light-emitting device according to any of claims 1 to 18, wherein the anode comprises one of indium-tin oxide, tin oxide or zinc oxide.

20. An organic light-emitting device according to any of claims 1 to 19, wherein the first layer of conductive cathode material is sputter deposited.

21. An organic light-emitting device according to any of claims 1 to 19, wherein the first layer of conductive material is evaporated.

22. An organic light-emitting device according to any of claims 1 to 21, wherein the second layer of conductive material is sputter deposited.

23. An organic light-emitting device according to any of claims 1 to 21, wherein the second layer of conductive material is evaporated.

24. A method of fabricating an organic light-emitting device, comprising the steps of:

forming a cathode for the device over a substrate, which step comprises forming a first layer of a conductive material of high conductivity over a substrate and forming a second layer of a conductive material having a low work function over the first layer of conductive material, wherein the first layer of conductive material is an opaque metallic layer and the second layer of conductive material is substantially thinner than the first layer of conductive material having a thickness of at most 5 nm, and comprises an elemental metal, an alloy or an intermetallic compound having a work function of at most 3.7 eV;

forming at least one layer of a light-emissive organic material over the cathode; and

forming an anode for the device over the at least one layer of organic material.

25. A method of fabricating an organic light-emitting device, comprising the steps of:

forming an anode for the device over a substrate;

forming at least one layer of a light-emissive material over the anode; and

forming a cathode for the device over the at least one layer of organic material, which step comprises forming a second layer of a conductive material having a low work function over the at least one layer of organic material and forming a first layer of a conductive material of high conductivity over the second layer of conductive material, wherein the first layer of conductive material is an opaque metallic layer and the second layer of conductive material is substantially thinner than the first layer of conductive material having a thickness of at most 5 nm, and comprises an elemental metal, an alloy or an intermetallic compound having a work function of at most 3.7 eV.

26. A method of fabricating an organic light-emitting device according to claim 24 or 25, wherein the second layer of conductive material has a thickness in the range of from 0.5 to 2 nm.

27. A method of fabricating an organic light-emitting device according to any one of claims 24 to 26, wherein the second layer of conductive material has a thickness of about 0.5 nm.

28. A method of fabricating an organic light-emitting device according to any one of claims 24 or 27, wherein the substrate comprises one of a glass or a plastics material.

29. A method of fabricating an organic light-emitting device according to claim 28, wherein the substrate comprises polyester, polycarbonate, polyimide or poly-ether-imide.

30. A method of fabricating an organic light-emitting device according to any of claims 26 to 29, wherein the anode comprises one of indium-tin oxide, tin oxide or zinc oxide.

31. A method of fabricating an organic light-emitting device according to any of claims 26 to 30, wherein the first layer of conductive material has a thickness in the range of from 100 to 500 nm.

32. A method of fabricating an organic light-emitting device according to claim 31, wherein the first layer of conductive material has a thickness of about 150 nm.

33. A method of fabricating an organic light-emitting device according to any of claims 26 to 32, wherein the first layer of conductive material comprises Al or an alloy thereof.

34. A method of fabricating an organic light-emitting device according to any of claims 24 to 33, wherein the second layer of conductive material comprises an elemental metal, an alloy or an intermetallic compound having a work function of at most 3.2 eV.

35. A method of fabricating an organic light-emitting device according to any of claims 24 to 34, wherein the second layer of conductive material comprises one of an alkali metal, an alkaline

earth metal or a lanthanide, or an alloy or an intermetallic compound thereof.

36. A method of fabricating an organic light-emitting device according to claim 35, wherein the second layer of conductive material comprises one of Ca, K, Li, Sm or an Al-Li alloy.

37. A method of fabricating an organic light-emitting device according to any of claims 24 to 36, wherein the ratio of thicknesses of the first layer of conductive material to the second layer of conductive material is at least 20 : 1.

38. A method of fabricating an organic light-emitting device according to any of claims 24 to 37, wherein the at least one layer of organic material has a thickness of about 100 nm.

39. A method of fabricating an organic light-emitting device according to any of claims 24 to 38, wherein the organic material is a conjugated polymer.

40. A method of fabricating an organic light-emitting device according to any of claims 24 to 38, wherein the organic material is a low molecular weight compound.

41. A method of fabricating an organic light-emitting device according to any of claims 24 to 38, wherein the at least one layer of organic material comprises a composite structure including at least one layer of a conjugated polymer and at least one layer of a low molecular weight compound.

42. A method of fabricating an organic light-emitting device according to any of claims 24 to 41, wherein the first layer of conductive material is sputter deposited, preferably by DC magnetron or RF sputtering.

43. A method of fabricating an organic light-emitting device according to any of claims 24 to 41, wherein the first layer of

conductive material is evaporated, preferably by resistive or electron-beam thermal evaporation.

44. A method of fabricating an organic light-emitting device according to any of claims 24 to 43, wherein the second layer of conductive material is sputter deposited, preferably by DC magnetron or RF sputtering.

45. A method of fabricating an organic light-emitting device according to any of claims 24 to 43, wherein the second layer of conductive material is sputtered, preferably by DC magnetron or RF sputtering.

46. An organic light-emitting device, comprising at least one layer of a light-emissive organic material arranged between an anode and a cathode for the device, wherein the cathode comprises a first layer of a conductive material which is a DC magnetron sputtered metallic layer of high conductivity and a second layer of a conductive material having a low work function arranged between the at least one layer of organic material and the first layer of conductive material, wherein the second layer of conductive material is substantially thinner than the first layer of conductive material.

47. An organic light-emitting device substantially as hereinbefore described with reference to the accompanying drawings.

48. A method of fabricating an organic light-emitting device substantially as hereinbefore described with reference to the accompanying drawings.

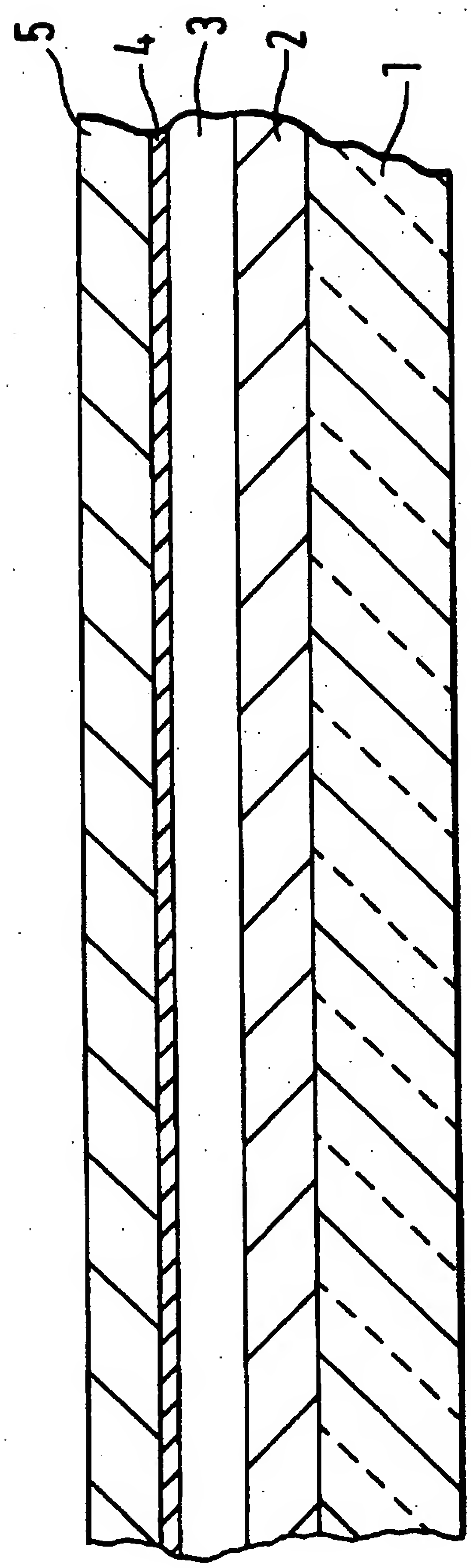

FIG. 1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 97/02380

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H05B33/26 H05B33/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H05B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	DATABASE WPI Section Ch, Week 9716 Derwent Publications Ltd., London, GB; Class A85, AN 97-171347 XP002048893 & JP 09 035 871 A (SUMITOMO CHEM CO LTD) , 7 February 1997 see abstract ---	1-3
X	EP 0 684 753 A (NEC) 29 November 1995 see the whole document ---	1-17, 19-23, 25-28, 30-42, 44-48

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1

Date of the actual completion of the international search	Date of mailing of the international search report
2 December 1997	23/12/1997

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Drouot, M-C

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication where appropriate, of the relevant passages	Relevant to claim No.
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